Master's Thesis

THE POTENTIAL OF HYDROLYZED URINE AS A SOLVENT FOR BIOGAS UPGRADING

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(Environmental Science and Engineering)

Graduate School of UNIST

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Abstract

The demand for sustainable energy production is increasing worldwide as the issue of climate change has come to the fore along with the constant increase of energy consumption. Consequently, growing attention has been directed toward the development and use of renewable energy sources. Anaerobic digestion (AD) is regarded as a promising renewable energy technology as it can be used to convert waste organic carbons to energy in the form of biogas. The potential of AD to reduce pollution loads while simultaneously producing energy makes it environmentally and economically appealing.

Biogas produced from AD is composed of approximately 60% (v/v) methane (CH_4) and 40 (v/v) carbon dioxide (CO_2), with other gases, including hydrogen sulfide comprising less than 1% (v/v). Although sufficient for use as fuel for boilers or generators, the relatively low CH_4 content (i.e., low calorific value) limits the direct use of biogas as a transportation fuel or a natural gas replacement. In order to improve the quality of biogas, it is necessary to remove CO_2, which has no energy content but comprises a large part, and other impurities so as to increase the CH_4 content. This process is called biogas upgrading, and in the context of energy content, the heart of biogas upgrading is the removal of CO_2. One of the most commonly used methods for biogas upgrading is chemical absorption using an aqueous alkaline solvent, and this process has been extensively employed for carbon capture and storage. Aqueous solutions of alkanolamines, such as monoethanolamine (MEA), are the most widely used solvents for chemical absorption in industrial-scale processes. Aqueous ammonia has been spotlighted as an alternative to MEA because it has 2–3-fold higher CO_2 absorption capacity than MEA and is not degraded by reaction with other gases such as SO_2, NO_2, or O_2. However, ammonia solution has a critical drawback in that the loss of ammonia is inevitable due to its high saturated vapor pressure and volatility, which reduces the economic feasibility of the overall absorption process. This problem can be circumvented by using an inexpensive and sustainable source of ammonia such as human urine.

Human urine contains approximately 2% (w/w) urea, and its hydrolysis produces approximately 4,000 mg/L of total ammonia nitrogen. This increases the pH of hydrolyzed urine to provide an alkaline environment favorable for CO_2 absorption. Given this background, this study aims to investigate the feasibility of using hydrolyzed urine as a CO_2 solvent for biogas upgrading. As the first step, urine hydrolysis was tested with different doses of urease (0, 5, 10, 20, and 30 mg/L) at 25℃. The pH of urine increased from 6.68 (in fresh urine) to 9.00 or higher within 20 hours in all runs performed with urease, whereas the run without urease addition showed no increase in pH during an experimental period of 68.5 hours. All urease-added runs eventually reached a similar pH of approximately 9.2; however, the conductivity and total ammonia nitrogen (TAN) concentration at the

end of the experiment indicated that complete ureolysis was not achieved in the run performed with 5 mg/L urease. This implies that the pH did not adequately reflect the level of ureolysis. Subsequently, urine was hydrolyzed with and without urease (10 mg/L) addition at different temperatures (4, 25, and 35℃) to investigate the effect of temperature. A higher temperature induced an increased ureolysis rate regardless of the addition of urease, and this effect was much more pronounced in the runs without urease. Periodical monitoring of conductivity and pH throughout the experiment for 60 days confirmed that pH is not a reliable indicator of ureolysis, but conductivity is.

Hydrolyzed urine (with 10 mg/L urease at 25℃ over 5 days) was tested for biogas upgrading in batch mode using a synthetic gas mixture of 60% CH_4 and 40% CO_2 (v/v). The CH_4 content increased to approximately 80% when 5 L of the synthetic biogas was treated with 400 mL of hydrolyzed urine, but reached only 70% when the loaded biogas volume was doubled. The biogas upgrading rate (i.e., the rate of CH_4 increase or CO_2 decrease) increased with increasing gas circulation rate (20, 50, and 80 mL/min), which had no significant effect on the final CH_4 content. The pH of hydrolyzed urine decreased to near neutral levels with the absorption of CO_2. The pH and CO_2 content showed very similar profiles during the biogas upgrading tests, and a significant linear relationship between them was identified. This means that the pH of urine can be used as a convenient indicator of the biogas upgrading process. An experiment using 5 L of real biogas produced from lab-scale digesters (62% CH_4 and 38% CO_2 (v/v)) was performed at a circulation rate of 50 mL/min, and a similar upgrading performance as that obtained with the test using the synthetic biogas was achieved. The CH_4 content reached saturation at 80% in 4 hours, and additionally 2700 ppmv of H_2S present in the real biogas was completely removed. The overall results demonstrated that hydrolyzed urine can be effectively used as a solvent for upgrading biogas. Although further studies to develop and optimize the process for continuous operation are required for practical implementation, this technique offers a new way to valorize human urine. Ammonia in urine can react with absorbed CO_2 and form NH_4HCO_3, a valuable fertilizer material. However, although the reason is not clear, the formation of NH_4HCO_3 during biogas upgrading in the present study was not confirmed by X-ray spectroscopy or diffraction analyses. Optimizing the formation and recovery of NH_4HCO_3 may provide a way to further improve the economy of the urine-based biogas upgrading process and thus the value of human urine.

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Chapter 1. Introduction

1.1. Anaerobic digestion

Climate change is undoubtedly caused by human activities, especially the utilization of fossil fuels. Fossil fuels accounted for approximately 81.7% of the primary energy supply in 2012, whereas non-fossil resources only contributed 13.5%. With energy consumption growing at about 2.3% per year (Ellabban et al., 2014), new renewable energy sources to replace fossil fuels and simultaneously reduce the adverse environmental impact have attracted a lot of attention all over the world.

Among the various renewable energy resources available, such as wind energy, solar energy, hydro energy, geothermal energy, and bio energy, bio energy is the only energy source capable of producing liquid fuels other than electricity or heat (Jung et al., 2016, Ellabban et al., 2014). In addition, bio energy is one of the most promising future renewable energy sources because it guarantees continuous power generation, unlike other types of renewable energy such as solar and wind energy (Appels et al., 2011).

Technologies based on bio energy can be divided into thermochemical, biochemical, and physicochemical conversion processes. Anaerobic digestion (AD) is a biochemical conversion process and is considered a promising renewable energy technology for managing organic wastes as it can recover energy in the form of biogas while reducing pollution loads. AD is a multi-step process in which the microbiological, biochemical, and physicochemical aspects are closely linked (Angelidaki et al., 2009). The AD process involves hydrolysis, acidogenesis, acetogenesis, and methanogenesis, as shown in Figure 1. In the hydrolysis process, complex organic materials such as carbohydrates, proteins, and/or fats are broken down into soluble organics, sugars amino acids, and fatty acids by hydrolytic fermentative bacteria. After hydrolysis, soluble organics are further broken down and volatile fatty acids (VFAs) are produced during acidogenesis along with other by-products such as NH_3, CO_2, and H_2S. The third stage is the acetogenesis process, where higher organic acids and alcohols produced by acidogenesis are further treated with acetogens to produce mainly acetic acids as well as CO_2 and H_2 (Appels et al., 2008). Finally, methane (CH_4) and carbon dioxide (CO_2) can be produced by two groups of methanogenic bacteria during the methanogenesis process: acetoclastic and hydrogenic-utilizing methanogens.

The biogas produced through AD is energy efficient and environmentally friendly due to the low emission of hazardous pollutants (Appels et al., 2011). AD can be applied to biomass sources containing high water content without any pre-treatments. In contrast, other technologies such as pyrolysis and gasification require an additional pre-drying step because their efficiency decreases significantly as the water content increases. Moreover, the slurry (i.e. digestate) produced from AD

can be utilized as a nutrient fertilizer and AD can be applied in both large and small scale.

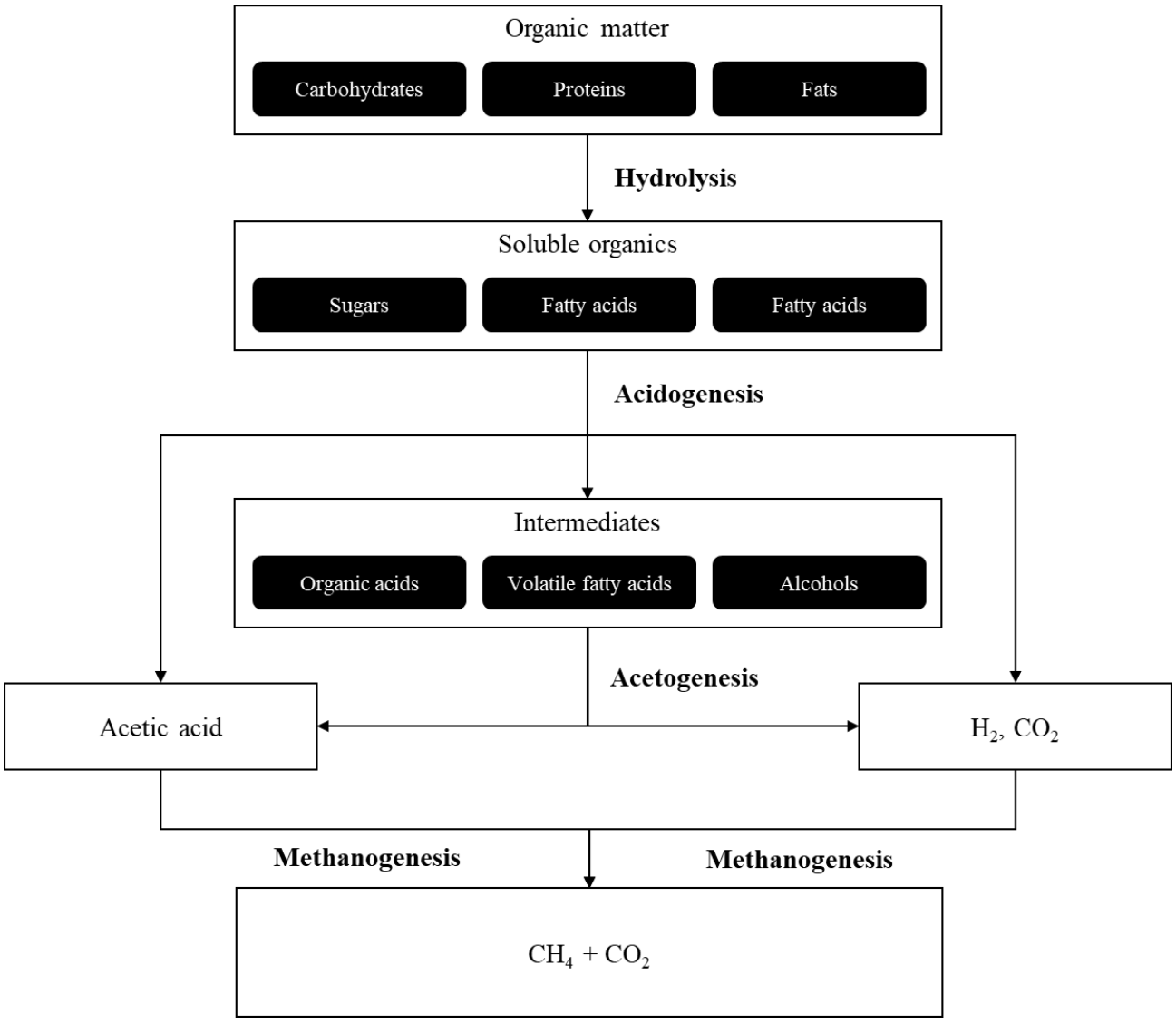


Figure 1. Multi-phase stages in the anaerobic digestion process

1.2. Biogas upgrading

Unlike CH_4, which can be used as energy for heat or electricity, all other gases in biogas such as CO_2, nitrogen (N_2), hydrogen sulfide (H_2S), vapor water (H_2O), and ammonia (NH_3) are unwanted products of AD and considered contaminants (Angelidaki et al., 2018). CO_2 has no energy content unlike CH_4 but occupies the largest portion of by-product from AD, comprising typically 30–50% of the total biogas. CO_2 is the greatest contributor to the greenhouse effect among the group of greenhouse gases produced by human activities (IPCC, 1990). Additionally, biogas must be upgraded for use as standard natural gas (i.e. biomethane). Consequently, biogas upgrading is a meaningful process performed by removing or converting CO_2 to CH_4 (Kougias et al., 2017).

Several technologies have been developed specifically for the removal of CO_2 from biogas, including chemical absorption, physical adsorption, membrane separation, water scrubbing, pressure swing adsorption (PSA), and biological technologies. Among these, chemical absorption is one of the most commonly used methods for upgrading biogas and is known to result in negligible CH_4 loss (< 0.1) compared to the other technologies (Angelidaki et al., 2018, He et al., 2017). For comparison, water scrubbing and PSA can result in CH_4 loss as high as 2–20%. Minimizing CH_4 loss is essential because its global warming potential (GWP) value relative to CO_2 for a 100-year time period is estimated to be 28, which means that CH_4 has 28 times higher potential than CO_2 to deteriorate the global warming effect (Pachauri et al., 2014). Another advantage of chemical absorption is that it requires a relatively low cost to reduce CO_2 emission (Chakma et al., 1995).

Chemical absorption has been extensively utilized for carbon capture storage (CCS) with principles similar to those of biogas upgrading and alkanolamines, especially monoethanolamine (MEA) are most widely used for the process in industrial settings. The CO_2 absorption efficiency of MEA has been reported to be higher than 90% (Veawab et al., 2002). The chemical reaction between CO_2 and alkanolamine is described by the following Equation 1 (Blauwhoff et al., 1983):

$$R_3N + CO_2 + H_2O \leftrightarrow R_3NH^+ + HCO_3^- \quad (1)$$

The CO_2 capture mechanism by MEA is described in Equation 2 (Gray et al., 2005):

$$C_2H_4OHN_{2\,(l)} + CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow C_2H_4OHNH_3^+{}_{(aq)} + HCO_3^-{}_{(aq)} \quad (2)$$

However, the implementation of MEA scrubbing has some limitations: (1) MEA solvent has low CO_2 absorption capacity, (2) high operating cost is needed, (3) high specific energy is required for

regeneration of CO_2, (4) degradation of MEA might occur through a reaction with existing SO_2, NO_2, and O_2, resulting in solvent loss and corrosion, (5) amine degradation compounds, nitrosamines, and nitramines are potentially harmful to humans, and (6) the regeneration of MEA is necessary because it is an expensive material (Leung et al., 2014, Mani et al., 2006, McLeod et al., 2014, Yeh and Bai, 1999).

Aqueous ammonia has been recently highlighted as an attractive alternative to MEA since it does not degrade or corrode and requires much lower energy for regeneration. In addition, it was reported several times that aqueous ammonia has 2–3 times higher CO_2 absorption capacity than MEA (Mani et al., 2006, Yeh and Bai, 1999, Yeh et al., 2005). The reason for the higher CO_2 capacity for aqueous ammonia compared to MEA is that the carbamate equilibrium constant for MEA is much higher than that for ammonia, suggesting ammonia derived carbamate is formed with a lower yield than the equivalent MEA derived carbamate (Herri et al., 2014).

Possible reactions in the CO_2-NH_3-H_2O system are presented in the following equations (Bai and Yeh, 1997, Meng et al., 2005):

$$CO_{2\,(g)} + 2NH_{3\,(g)} \leftrightarrow NH_2COONH_{4\,(s)} \quad (3)$$

$$NH_2COONH_{4\,(s)} + H_2O_{\,(g)} \leftrightarrow (NH_4)_2CO_{\,(s)} \quad (4)$$

$$CO_{2\,(g)} + 2NH_{3\,(g)} \leftrightarrow CO(NH_2)_{2\,(s)} + H_2O_{\,(g)} \quad (5)$$

$$CO_{2\,(g)} + 2NH_{3\,(aq)} \rightarrow NH_4^{+} + NH_2COO^{-}{}_{(aq)} \quad (6)$$

$$2NH_{3\,(g)} + CO_{2\,(g)} + H_2O_{\,(g)} \leftrightarrow (NH_4)_2CO_{3\,(s)} \quad (7)$$

$$NH_{3\,(g)} + CO_{2\,(g)} + H_2O_{\,(g)} \leftrightarrow NH_4HCO_{3\,(s)} \quad (8)$$

$$2NH_{3\,(l)} + CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow (NH_4)_2CO_{3\,(s)} \quad (9)$$

$$NH_{3\,(l)} + CO_{2\,(g)} + H_2O_{\,(l)} \leftrightarrow NH_4HCO_{3\,(s)} \quad (10)$$

The above reactions proceed under operating conditions. Ammonia carbamate (NH_2COONH_4) is the main product of the reaction of ammonia and carbon dioxide in dry conditions under ambient pressure (Equation 3). However, it is so freely soluble in water that it becomes ammonium carbonate ($(NH_4)_2CO_3$) under moist conditions (Equation 4). While under high pressure and high temperature (> 140°C), urea ($CO(NH_2)_2$) is directly produced (Equation 5). At room temperature and atmospheric pressure, the reactions presented in Equations 4 to 8 can occur and the forward reactions are dominant. The crystalline products are primarily composed of white ammonium bicarbonate (NH_4HCO_3), which has been employed by certain developing countries as a fertilizer for over 30 years (Budzianowski, 2012). However, the critical drawback of using ammonia as a solvent is the likelihood of ammonia volatilization due to the high saturated vapor pressure. As a result, significant economic loss is inevitable. Accordingly, studies on cheap and sustainable new ammonia sources such as human urine are needed to overcome the disadvantages of using aqueous ammonia as a solvent.

1.3. Human urine

Although nitrogen and phosphorus are essential nutrients to living things, large amounts of energy are required for the removal and recovery of nitrogen and phosphorus in wastewater treatment plants because they increase the risk of eutrophication of water when released in large quantities (Kuntke, 2013). Human urine contributes approximately 85% of nitrogen and 50% of phosphorus to the total domestic wastewater but only 1% of the total volume (Larsen et al., 2009, Zhang et al., 2013). In addition, urine contains micropollutants such as human pathogens which cause serious water problems. Thus, urine separation technologies (e.g. No-Mix toilet) have been extensively implemented along with technologies for efficient recovery of nutrients from urine (Larsen et al., 2009).

Approximately 85% of the nitrogen in fresh urine is fixed as urea (Udert et al., 2006) and the urea can be hydrolyzed by ubiquitous urease-positive bacteria (Zhang et al., 2013). According to Equation 11, hydrolysis of one mole of urea releases two moles of ammonia and one mole of carbonic acid (Mobley and Hausinger, 1989). These products decompose spontaneously to ammonium ion and bicarbonate ion as expressed in Equation 12.

$$NH_2(CO)NH_2 + H_2O \rightarrow 2NH_3 + H_2CO_3 \quad (11)$$

$$2NH_3 + H_2CO_3 + H_2O \rightarrow 2NH_4^+ + HCO_3^- + OH^- \quad (12)$$

This results in a net increase in the pH and conductivity of urine, which allows spontaneous precipitation of calcium, magnesium, phosphate, and ammonia ions in the form of struvite (MAP, $MgNH_4PO_4 \cdot 6H_2O$), hydroxyapatite ($Ca_5(PO_4)_3(OH)$), and calcite ($CaCO_3$) in the urine (Luther et al., 2015, Udert et al., 2006). Additionally, the increase in pH provides an alkaline environmental favorable for CO_2 absorption.

Urine hydrolysis can cause serious blockage problems in the urinary pipe due to upper mineral precipitation. Malodor can be released during urine hydrolysis; however, the ammonia released during human urine hydrolysis seems to be a decent alternative to alkanolamines and aqueous ammonia for capturing CO_2 in biogas. On average, humans excrete 1.4 L of urine daily with mean values ranging from 0.6 to 2.6 L (Rose et al., 2015). It has been reported several times that fully hydrolyzed urine can produce approximately 4,000 mg/L of total ammonia nitrogen (TAN), as summarized in Table 1. Consequently, it can be said that a person produces approximately 2 kg of ammonia nitrogen source per year. This is attractive enough to be a competitive and economical new source of aqueous ammonia for biogas upgrading due to no need to spend money. Several studies which focused on

nutrient rich slurry as a renewable source of aqueous ammonia for upgrading biogas have been reported (McLeod et al., 2014, He et al., 2017, He et al., 2018). However, there have been few studies which focused on hydrolyzed human urine as a new source of ammonia for biogas upgrading. Therefore, the potential to use human urine for upgrading biogas was examined in the current study.

Table 1. Summary of characteristics of the hydrolyzed urine in other studies

Way to hydrolyze the urine	pH	Conductivity (mS/cm)	COD (mg/L)	TAN (mg/L)	Mg^{2+} (mg/L)	Ca^{2+} (mg/L)	PO_4^{3-} (mg/L)	Reference
By adding urease	9.40	35.7	6500	4800	1.5	55.2	200	Liu et al. (2015)
	9.00	25.9					195	Etter et al. (2011)
By long storage	9.29	29.8		3073[a]			432	Triger et al. (2012)
	8.69		4500	2390	< 5	16	208	Udert and Wachter (2012)
	8.90	25.0	4500	2540[a]	1.6	16.5	197	Hug and Udert (2013)
	8.99		3460	3820				Tarpeh et al. (2017)

[a] NH_4^+-N concentration

1.4. Objectives

The objectives of this study were as follows:

(1) To investigate the hydrolysis behavior of human urine at different urease doses and temperatures

(2) To evaluate the potential use of hydrolyzed human urine as a carbon dioxide solvent for biogas upgrading

Chapter 2. Materials and Methods

2.1. Collection of fresh human urine

Fresh human urine samples were collected twice from nine healthy adult volunteers (five men and four women; age range, 23–27). The urine samples collected in April 2018 were designated as U1 and those collected in August 2018 were designated as U2. Without dilution with water, each collected urine sample was mixed well and stored in the refrigerator before the experiments. The collected urine samples are shown in Figure 2.

Figure 2. Collected fresh human urine sample

The average composition of the collected urine samples is given in Table 2. The conductivity of U1 was 9.35 mS/cm and the TAN was 71 ± 4 mg/L. However, the conductivity and TAN were higher in U2 than in U1. The conductivity of U2 was 10.77 mS/cm and TAN was 333 ± 3 mg/L. As a result, the conductivity and TAN were slightly different after complete hydrolysis, as shown in Table 3.

Table 2. Average composition of collected fresh human urine samples. U1 is previously collected urine sample (in April 2018); U2 is subsequently collected sample (in August 2018).

Parameters	Unit	U1	U2
pH		6.62	6.39
Conductivity	mS/cm	9.35	10.77
Alkalinity	as $CaCO_3$	1130	1210
COD	mg/L	4088 (438)[a]	3610 (13)
Cl^-	mg/L	2480 (20)	2372 (93)
NO_3^-	mg/L	269 (4)	132 (34)
PO_4^{3-}	mg/L	995 (1)	890 (23)
SO_4^{2-}	mg/L	749 (1)	822 (57)
Na^+	mg/L	1442 (11)	1313 (47)
Total ammonia nitrogen (TAN)	mg/L	71 (4)	333 (3)
K^+	mg/L	994 (8)	1133 (21)
Mg^{2+}	mg/L	27 (7)	133 (7)
Ca^{2+}	mg/L	224 (20)	347 (89)
Urea	mmol/L	nd[b]	145 (3)

[a] Standard deviations are in parentheses.
[b] Not detected.

Table 3. Conductivity and total ammonia nitrogen (TAN) after urea hydrolysis

After hydrolysis	Conductivity (mS/cm)	TAN (mg/L)
U1	22–23	4,000
U2	27–28	4,500

2.2. Urease

Jack bean urease (Type III, U1500, Sigma-Aldrich), which catalyzes the hydrolysis of urea, was used for all experiments to need. The specific activity of the urease was 15,000–50,000 units/g solid. One unit referred to the ability to liberate 1 μmole of ammonia from urea per minute at pH 7 and 25 ℃.

2.3. Effect of dose of urease on urine hydrolysis

The effect of the dose of urease on fresh human urine hydrolysis was tested by monitoring the pH in real time. Before the experiment, three assumptions were set: (1) The specific activity of the urease used was assumed to be 32.5 units/mg, which is the mean value of the specific activity range provided in the product information. (2) The urea concentration in human urine (g/g) was assumed to be 2%, which means that 200 mL of urine contained 4 g of urea. (3) There was no effect of increased pH on the urease activity.

The expected time to hydrolyze 200 mL of fresh urine depending on the amount of added urease was calculated and is presented in Table 4. Five concentrations of urease were selected for the simulation of urea hydrolysis: 0 (blank), 5, 10, 20, and 30 mg/L. The detailed experimental method is shown in Table 5. Briefly, 250 mL glass bottles were filled with 200 mL of the U1 urine samples. The temperature was not adjusted and the average temperature during the experiment was 26.0 ± 0.8℃. pH was recorded every 10 minutes during the first two hours and every 30 minutes thereafter. All conditions were tested in triplicate. After the experiment, conductivity and TAN were measured.

Table 4. Expected hydrolysis time for fully hydrolysis of 200 mL of human urine

Amount of urease (mg/L)	Expected time (hour)
5	68.7
10	34.4
15	22.9
20	17.2
25	13.7
30	11.5

Table 5. Summary of experimental method

Parameters	Conditions
Source of urine	U1
Volume	200 mL urine in 250 mL glass bottles
Temperature	Not adjusted (26.0 ± 0.8℃)
Amount of urease	0 (Blank), 5, 10, 20 and 30 mg/L
Measurements	pH recorded every 30 minutes
Repeat	In triplicate (Total 15 bottles)

2.4. Urine hydrolysis test under various conditions

The degree of hydrolysis of the fresh human urine was tested by measuring pH and conductivity daily under various conditions, three different temperatures (4, 25, and 35℃) and the presence or absence of urease. During the first 48 hours, pH and conductivity were measured every 4 hours only for samples with added urease. The 4℃ condition represents storage in the refrigerator, whereas 25℃ represents storage at room temperature and 35℃ is the temperature commonly employed for the mesophilic digestion process (Nallathambi Gunaseelan, 1997). For the experiment, 100 mL glass bottles filled with 100 mL of fresh urine sample (U2) were used and all conditions were tested in duplicate, for a total of twelve bottles. Urease was added at 10 mg/L of urine based on the results from previous experiments. The concentrations of TAN and urea were measured at 2 days for samples with added urease and at 60 days for all samples. The experimental method is summarized in Table 6.

Table 6. Summary of experimental method

Parameters	Conditions
Source of urine	U2
Volume	100 mL urine in 100 mL glass bottles
Temperature	4, 25, 35℃
Amount of urease	0, 10 mg/L
Measurements	pH and conductivity daily
Repeat	In duplicate (Total 12 bottles)

2.5. Biogas upgrading test using fully hydrolyzed urine

The viability of using hydrolyzed urine to capture carbon dioxide from biogas was tested in batch mode, and the schematic diagram is shown in Figure 3. A 10 L dual cork gas bag (350 mm × 500 mm) was filled with simulated gas and duplicate 500 mL glass bottles filled with 400 mL of hydrolyzed urine sample were used as the absorption reactor. A magnetic bar was used for stirring. Before introducing the biogas, N_2 was flowed toward the reactor at a flow rate of 50 mL/min for 10 minutes to purge unknown gases.

Before the experiments, fresh human urine (U2) was fully hydrolyzed with 10 mg/L of urease at room temperature over 5 days. The pH was 9.21 and conductivity was 27.42 mS/cm after hydrolysis, indicating that the urine sample was sufficiently hydrolyzed compared with previous experimental results.

For simulation of the biogas, synthetic biogas, which consisted of 60% CH_4 and 40% CO_2, was used at first. Afterward, real biogas, with an initial composition of 62% CH_4 and 38% CO_2 with 2,700 ppmv of H_2S, was tested to confirm that the use of real biogas was feasible. The real biogas came from a lab scale anaerobic digester which had been operated to digest mixed food waste and cabbage. Forty days of hydraulic retention time (HRT) and 2.5 g VS/L/day of organic loading rate (OLR) were applied to this anaerobic digester.

A summary of the experimental conditions is presented in Table 7. Different circulation rates (20, 50, and 80 mL/min) and volumes of biogas (5 and 10 L) were applied to the synthetic biogas. Only one condition (Circulation rate of 50 mL/min and 5 L biogas) was applied to the real biogas. The gas composition was measured every hour using an infrared biogas analyzer (Biogas 5000, Geotech). During analysis, the gas stream was not circulated through the reactor but was passed through the gas analyzer for five minutes. The pH and temperature were also recoded when the gas was analyzed. All tests were conducted under room temperature and atmospheric pressure.

After the biogas upgrading tests, solid products in the absorption reactor were collected and dried at 60℃ for a day to remove the supernatant. Scanning electron microscopy (SEM) coupled with energy-dispersive X-ray (EDX) was used to characterize the crystalline products from the test with hydrolyzed urine. In addition, high power X-ray diffraction (HP-XRD) was conducted for qualitative analysis of the crystalline products.

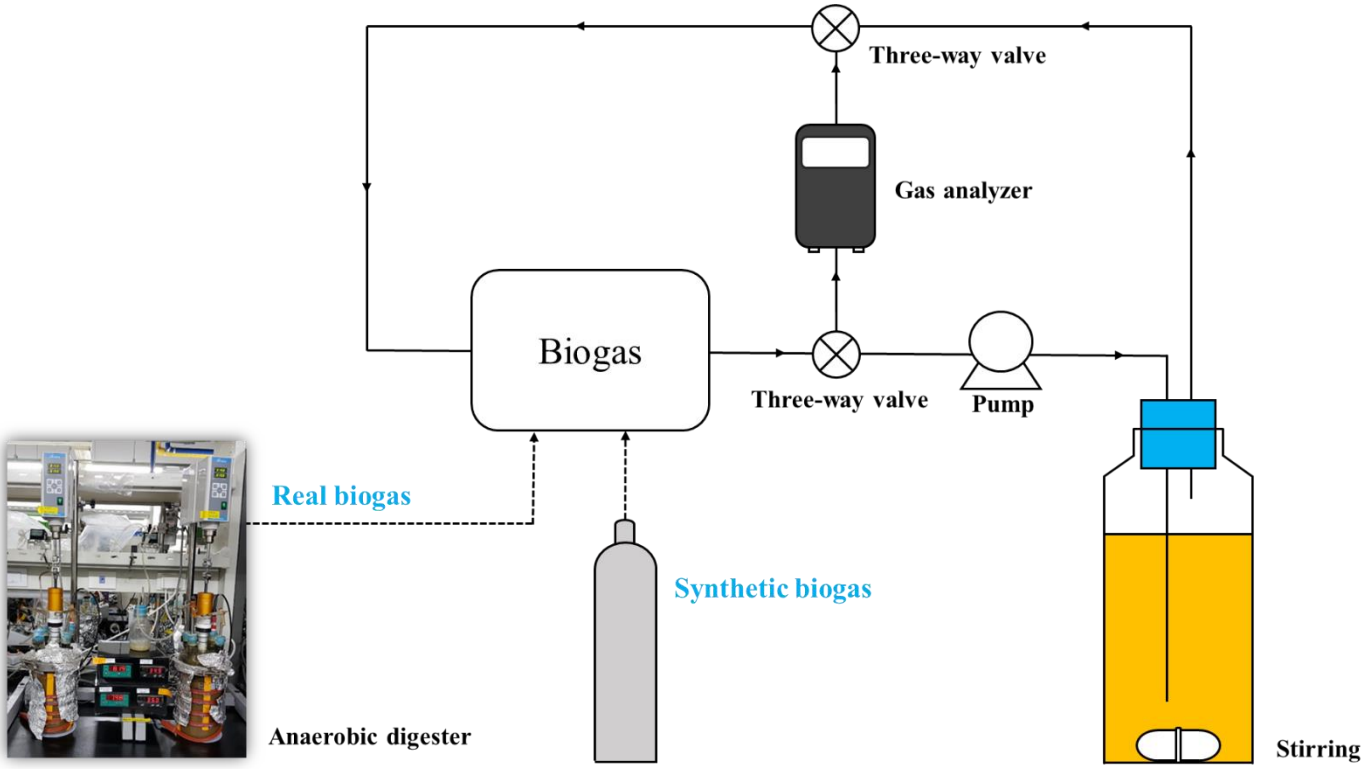


Figure 3. Schematic diagram of experiment for biogas upgrading in batch mode

Table 7. Experimental conditions for biogas upgrading test

Gas Volume	Biogas type	Urine volume	Circulation rate
10 L	Synthetic	400 mL	20 mL/min
			50 mL/min
			80 mL/min
5 L	Synthetic	400 mL	20 mL/min
			50 mL/min
			80 mL/min
5 L	Real	400 mL	50 mL/min

2.6. Analytical methods

A pH meter (ORION 3-Star, Thermo Scientific) was used for pH measurements. Alkalinity was determined using the ORION total alkalinity test kit (Thermo Scientific) and electrical conductivity was measured using the Orion Dual Star Multiparameter Meter and Orion Star A212 conductivity probe (Thermo Scientific). Anions and cations along with the TAN were analyzed using two Dionex ICS-1100 ion chromatographs (Thermo Scientific) coupled with an IonPac CS12A column (Thermo Scientific). Before measuring the ions, the samples were filtered through a 0.22 um pore membrane filter. Urea concentration was determined via a coupled enzyme reaction, which resulted in a colorimetric product (570 nm) proportional to the amount of urea present, using a urea assay kit (MAK 006, Sigma-Aldrich) and a spectrophotometric multi-well plate reader (Victor X3, Perkin Elmer) according to the manufacturer's protocols. The hydrogen sulfide content in real biogas was determined using a 490 Micro GC (Agilent). The stripped ammonia gas concentration was determined using a proper range of detector tubes and a gas collector (GV-100S, GASTEC). All measurements were performed at least in duplicate except for pH, alkalinity, and conductivity.

2.7. Statistical analysis

Two-way Analysis of Variance (ANOVA) was performed to examine significant differences in the factors involved in the biogas upgrading test, such as pH, gas contents and biogas volume. Analysis was performed with Microsoft Excel 2016 version.

Chapter 3. Result and Discussions

3.1. Effect of dose of urease on urine hydrolysis

pH variations along with the dose of urease during urine hydrolysis under room temperature (26.0 ± 0.8°C) are presented in Figure 4. The pH for all samples except for the blank sample (no added urease) increased as soon as the experiment started. The pH values for each sample at 2 hours were: 6.66 (0 mg/L), 8.22 (5 mg/L), 8.55 (10 mg/L), 8.81 (20 mg/L), and 8.92 (30 mg /L). These pH values correlated to a certain extent with the amount of urease. Moreover, the expected hydrolysis times were quite similar to the estimated times to reach the stationary state, as seen in Table 8. For example, the expected time was 68.7 hours and the estimated time to reach the stationary pH profile was 60–62 hours for samples with 5 mg/L urease added. The expected and estimated times to reach a stationary pH profile was 11.5 and 15–17 hours for the samples with 30 mg/L urease added, respectively. Based on the results, it appears possible to monitor the progress of urine hydrolysis through the pH profile and all urine samples with added urease seemed to be fully hydrolyzed during the experimental period of 68.5 hours.

However, the conductivity and TAN concentration, which were measured as soon as the experiments were over, indicated that all urine samples with added urease were not fully hydrolyzed, which was unexpected. Although all the pH values for the urine samples with added urease were almost the same at 9.14, the conductivity and TAN of the samples with 5 mg/L urease added were much lower than those of the other urine samples, as shown in Table 9. The conductivity was measured as 18.6 mS/cm in urine samples with 5 mg/L urease added, whereas the conductivity of urine with more urease ranged from 21.5 to 21.6 mS/cm, similar to the conductivity measured in the preliminary hydrolysis test shown in Table 3. TAN was approximately 2,900 mg N/L for the urine samples with 5 mg/L urease added and approximately 3800 mg N/L for the other samples.

Ammonia concentration is known to increase with the degradation of urea. Accordingly, it can be concluded that the urine sample with 5 mg/L urease added was not fully hydrolyzed although the pH value was similar to that of the other conditions. In addition, it has been reported that conductivity is a simple and effective measurement for tracking the extent of urea hydrolysis due to its linear correlation with ammonia. However, pH is not an effective measurement for examining the extent of urea hydrolysis because there is no correlation with the produced ammonia. Rather, pH measurement can be regarded as an indicator of the occurrence of hydrolysis (Ray et al., 2018).

A subsequent experiment was conducted by measuring the conductivity to investigate the effects of temperature and the presence of urease on urea hydrolysis. For this experiment, 10 mg/L urease was

used because this concentration was the smallest amount that could be used to achieve fully hydrolyzed urine.

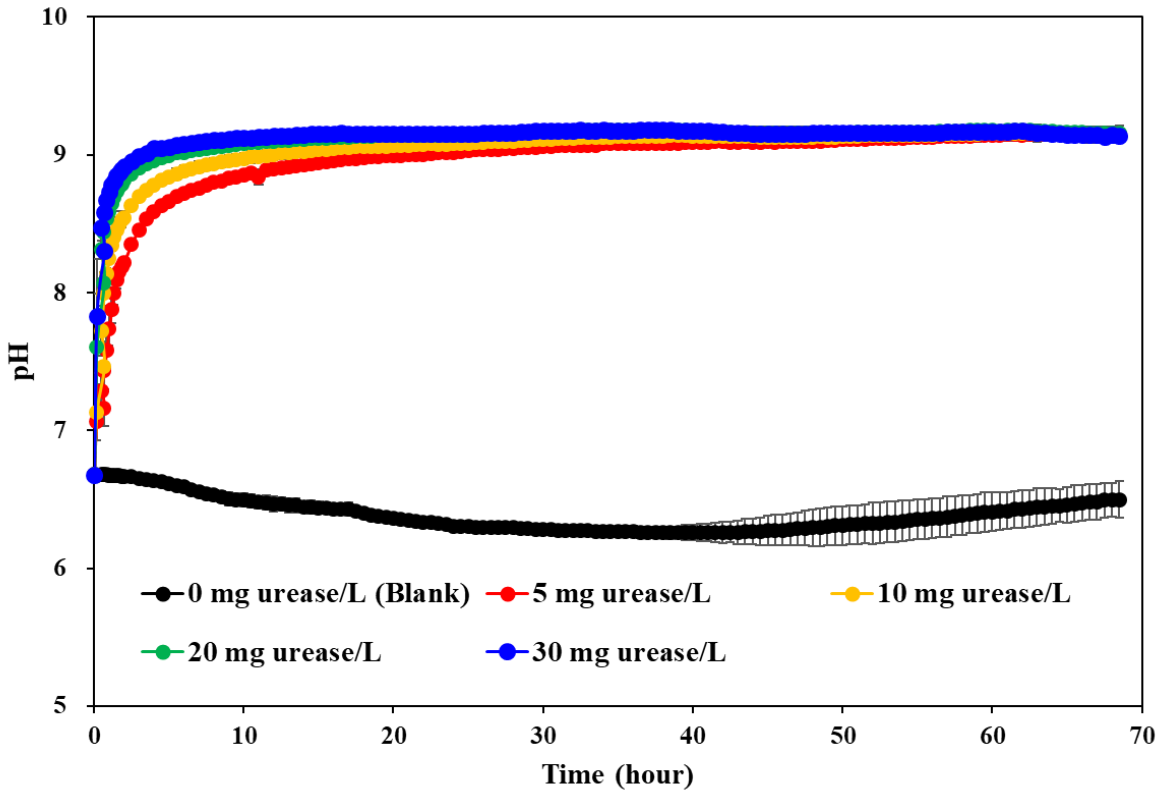


Figure 4. pH profile variations during urine hydrolysis. All pH measurements are presented in triplicate (n = 3) except for pH of sample added 5 mg urease/L (Red) in duplicate (n = 2) due to its wrong pH calibration.

Table 8. Comparison between the expected hydrolysis time and estimated time to reach plateau of pH

Amount of urease (mg/L)	Expected time (hour)	Time to reach plateau of pH (hour)
5	68.7	60–62
10	34.4	37–39
20	17.2	23–25
30	11.5	15–17

Table 9. Measurements at the end of the experiment with different dose of urease

Dose of urease (mg/L)	pH	Conductivity (mS/cm)	TAN (mg/L)
0	6.50 (0.13)[a]	9.85 (0.16)	250 (29)
5	9.15 (0.01)[b]	18.63 (0.43)	2913 (106)
10	9.15 (0.07)	21.64 (0.21)	3778 (108)
20	9.15 (0.02)	21.45 (0.35)	3793 (65)
30	9.14 (0.02)	21.50 (0.15)	3793 (100)

[a] Standard deviations are in parentheses (n = 3).
[b] Only presented in duplicate (n = 2) due to its wrong pH calibration

3.2. Hydrolysis of urine under different conditions

3.2.1. Urine hydrolysis process during the first 48 hours

As mentioned earlier, urea can be hydrolyzed to produce two ammonium ions and one bicarbonate, which results in elevated pH and increased ionic concentrations. Conductivity, which is related to the sum of the ionic strengths, was reported to be a simple indicator of the extent of urea hydrolysis due to its correlation with the concentration of ammonia and urea (Ray et al., 2018). Figure 5 presents the changes in pH profile and conductivity during the first 48 hours of urine hydrolysis under different temperatures. Hydrolysis of urine samples performed with no urease hardly occurred during the first 48 hours regardless of the temperature (4, 25 and 35℃) because there were almost no variations in the pH profile and conductivity as seen in Figure 5.

On the contrary, pH and conductivity immediately increased in the urine samples with added urease. According to Figure 5 A, the pH of all samples with urease sharply increased during the first 4 hours and hardly varied after 12 hours regardless of the temperature. However, the conductivity of these samples steadily increased during 48 hours of urine hydrolysis. Additionally, the conductivity of the urine sample with added urease was greatly affected by the temperature in the early stage of hydrolysis and the conductivity increased more rapidly in higher temperature conditions. Consequently, the presence of the urease caused the fresh urine to hydrolyze instantly.

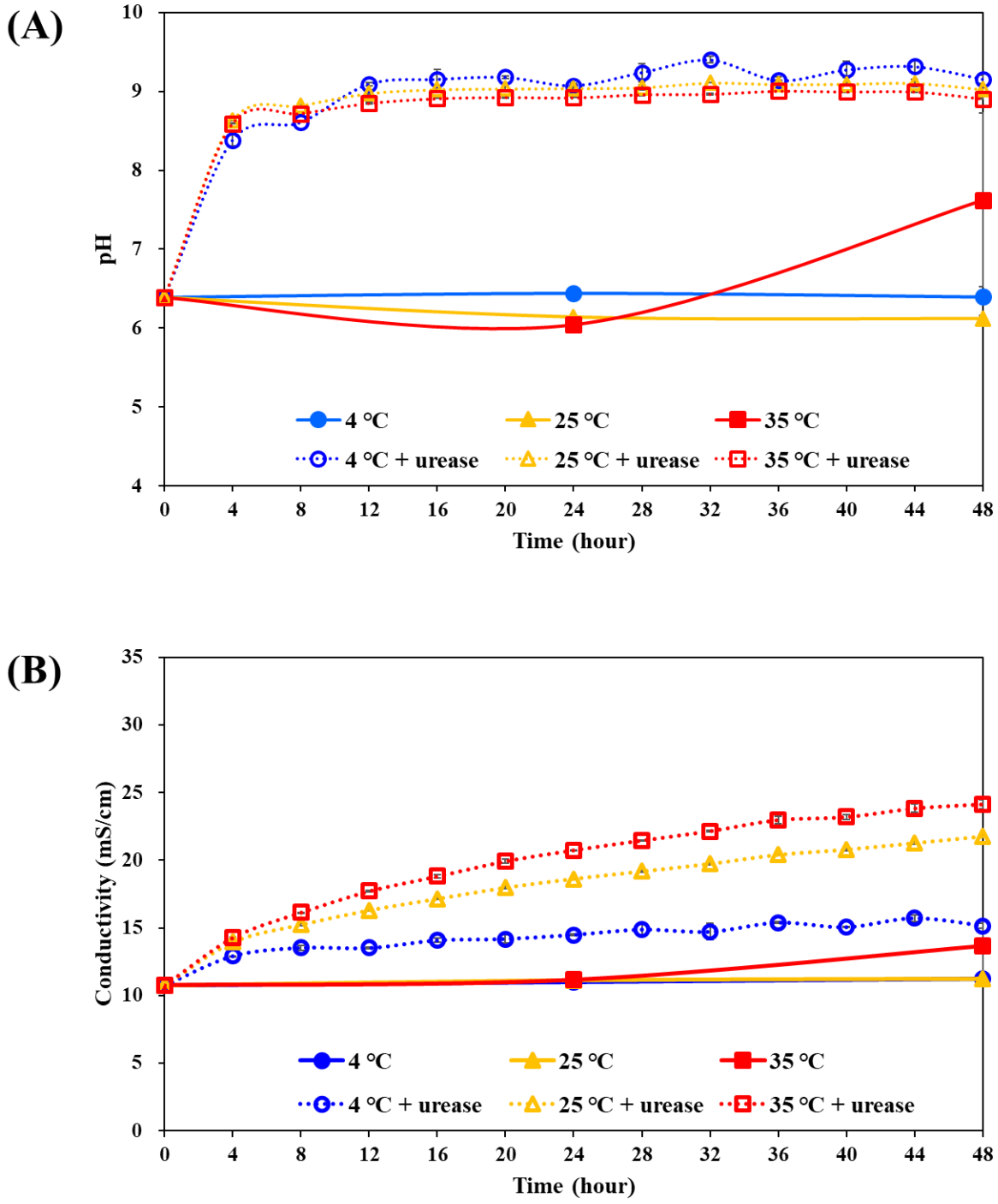


Figure 5. Variations of pH (A) and conductivity (B) during the first 48 hours

3.2.2. Urine hydrolysis process for 60 days

pH and conductivity were monitored for 60 days during urine hydrolysis test. The conductivity of the urine samples with added urease plateaued after five days at 25 and 35℃. However, the conductivity of the sample at 4℃ reached a stationary state after twelve days. This might be because the activity of the urease decreased as the temperature decreased. Therefore, it is a good idea to use room temperature as the operating temperature if the purpose is to hydrolyze the urine by using urease because there is little difference between urine hydrolysis at 25 and at 35℃. Moreover, refrigeration did not prevent the activity of urease completely.

Although the conductivity of hydrolyzed urine with urease was similar at 27–28 mS/cm, higher pH values were observed at lower temperatures. The average pH values for samples in the plateaued state at 4, 25, and 35℃ were 9.31 ± 0.12, 9.06 ± 0.07, and 8.87 ± 0.09. This result can be explained by equations 13–15 (Emerson et al., 1975). The pK_a of ammonium ion increased as the temperature decreased. For example, the pK_a value was 9.93 at 4 ℃ but 9.24 at 25℃ and 8.94 at 35℃. Consequently, pH would be higher at lower temperatures if the total ammonia concentration is the same.

$$NH_4^+ \leftrightarrow NH_3 + H^+ \quad (13)$$

$$pH = pK_a + \log[NH_3]/[NH_4^+] \quad (14)$$

$$pK_a = 0.09018 + 2727.92/T \quad (15)$$

For urine samples with added no urease, temperature had a more dynamic effect on the urine hydrolysis than the hydrolysis process performed with urease. According to Figure 6 A, the pH of urine at 35℃ increased immediately and reached a stationary state first (~10 day). The pH of urine at 25℃ increased after about a 6-day lag phase and reached a stationary state after about 21 days. Unlike the other temperature conditions, the pH of urine at 4℃ did not increase radically during the entire experimental period. Rather, it increased gradually from 6.4 to 7.2.

Conductivity increased similar to pH as seen in Figure 6 B. The conductivity of urine at 35℃ increased immediately with a small lag phase and reached a stationary state after 18 days. The pH of urine at 25℃ increased gradually after a 7-day lag phase and the increase continued until the experiment ended (~ 60 days). The conductivity of urine at 4℃ seemed to be unchanged, only increasing from 10.8 mS/cm to 11.1 mS/cm over 60 days.

From these experiments, it can be suggested that different strategies can be applied to urine

hydrolysis, considering the employed time and the length of the continuous process. In other words, the best strategy to hydrolyze urine with urease under room temperature or without urease under higher temperatures (> 35℃) would be a short retention time process. On the other hand, the best strategy to hydrolyze urine without using urease under room temperature would be a long retention time process. It would also be a good idea to keep the urine cold to prevent the loss of nitrogen in the event of a long transportation period.

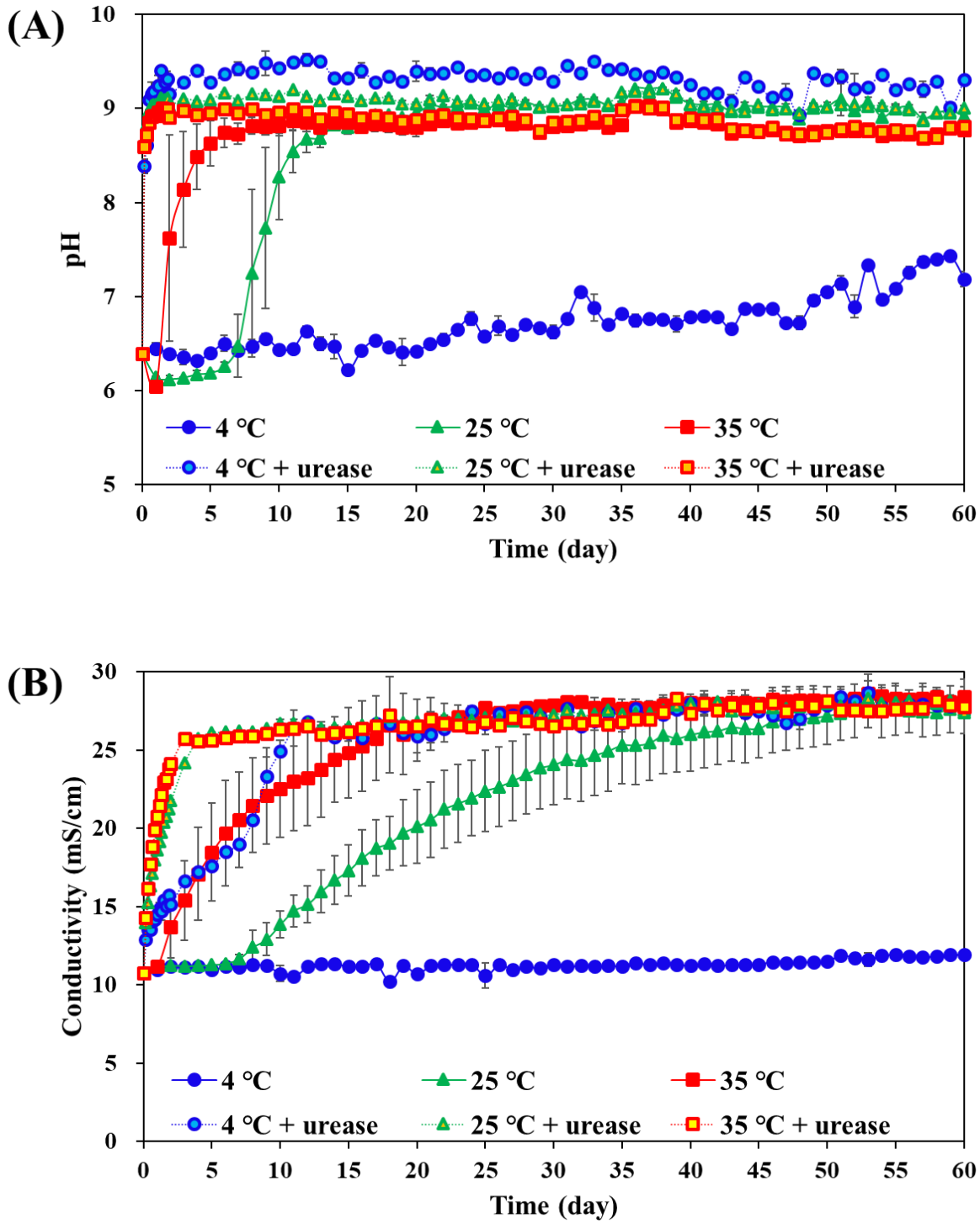


Figure 6. pH (A) and conductivity (B) variations for the entire experimental periods

3.2.3. Conductivity, TAN, and urea concentration

The average conductivity, TAN, and urea concentration at 0, 2, and 60 days are shown in Table 10. The concentrations of TAN and urea were measured at 2 days for samples with added urease and at 60 days for all samples. It was easily observed that conductivity had a positive correlation with TAN and a negative correlation with the urea concentration, as seen in Figure 7.

The conductivity and TAN of urine samples with added urease were higher at higher temperatures after 2 days. Nearly 90% of urea was degraded at 35℃, while only 50% was degraded at 4℃.

At 60 days, all the urea in the urine samples with added urease appeared to be fully degraded (> 95%). Urine samples with no added urease stored in the 4℃ refrigerator had nearly similar concentrations of urea as they did on day 0. This confirmed that urea is stable in cold conditions.

Table 10. Change in conductivity, TAN and urea concentration over time

Days	Samples	Conductivity (mS/cm)	TAN (mg/L)	Urea (mmol/L)
0	Fresh urine	10.77	337 (3) [a]	145.48 (3.27)
2	4℃ + urease	14.49 (0.05)	1527 (13)	69.11 (0.12)
	25℃ + urease	18.62 (0.07)	2538 (16)	35.96 (5.64)
	35℃ + urease	20.74 (0.03)	3035 (40)	19.13 (9.75)
60	4℃ + urease	27.62 (0.16)	4416 (121)	7.18 (1.07)
	25℃ + urease	27.36 (0.10)	4592 (27)	3.81 (0.80)
	35℃ + urease	27.74 (0.25)	4447 (426)	6.85 (3.05)
	4℃	11.91 (0.16)	393 (89)	143.37 (1.49)
	25℃	27.56 (1.49)	4493 (313)	14.62 (2.75)
	35℃	28.39 (1.15)	4676 (200)	11.90 (2.43)

[a] Standard deviations are in parentheses.

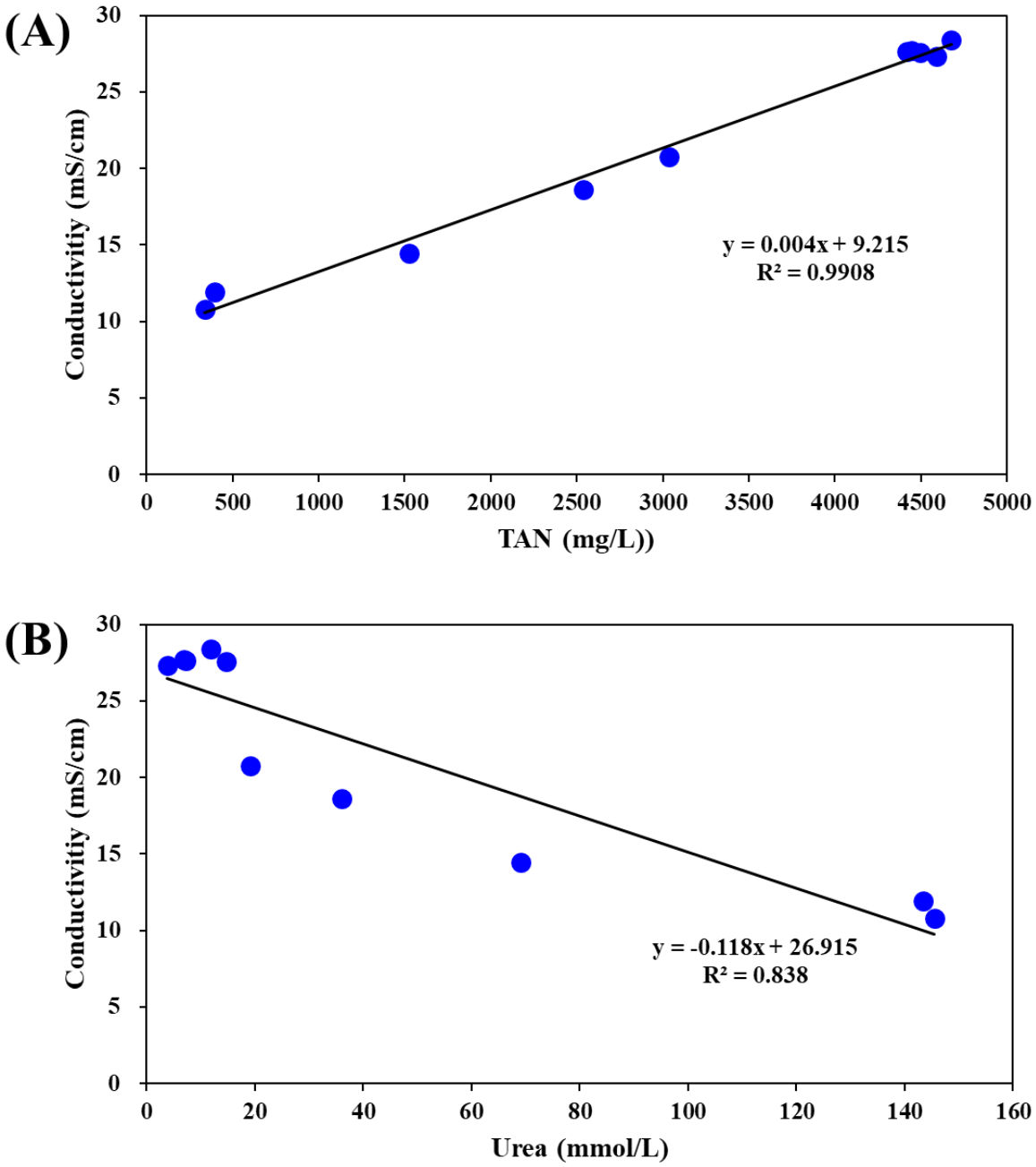


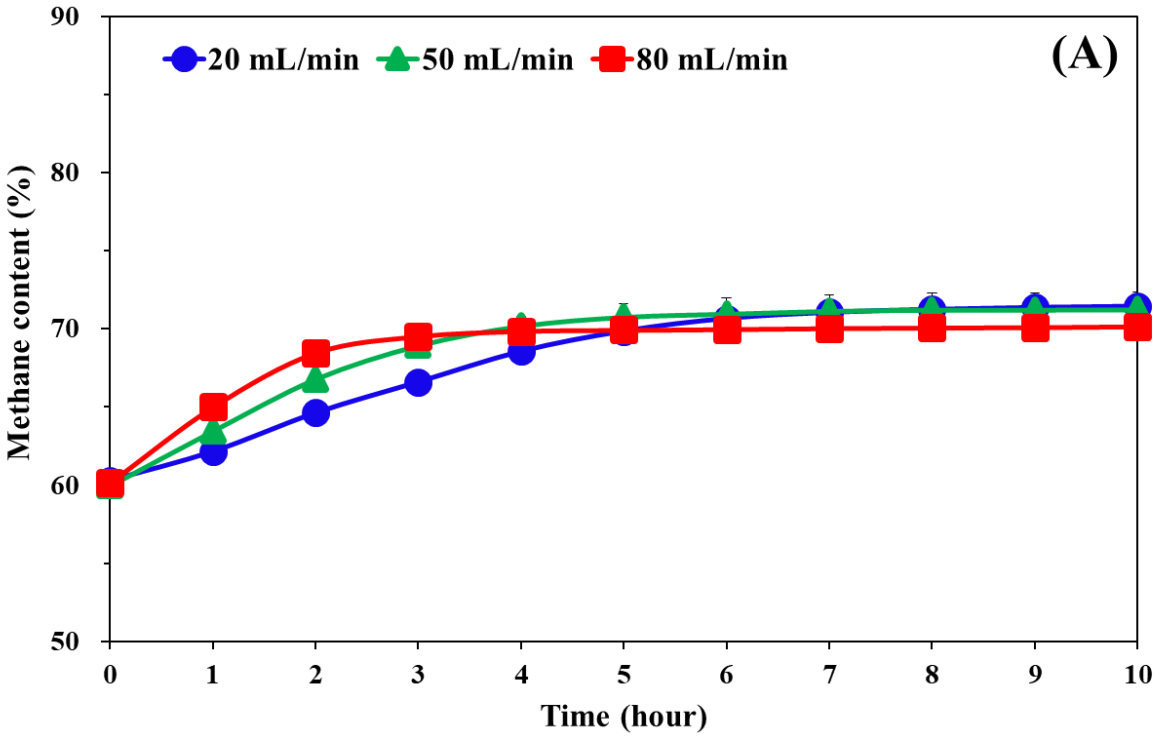
Figure 7. Conversion graph for total ammonia nitrogen and conductivity (A). Conversion graph for urea concentration and conductivity (B)

3.3. Batch test for biogas upgrading using hydrolyzed urine

3.3.1. Upgrading synthetic biogas

The gas composition (%) and pH variation during the treatment of 10 L of synthetic biogas with hydrolyzed urine are shown in Figure 8. The gas circulation rate seemed to affect the speed of the CH_4 upgraded. In other words, the CH_4 content reached the plateau state faster when a higher circulation rate was applied, as seen in Figure 8 A. Biogas treated with a circulation rate of 20 mL/min plateaued in 8–9 days, while biogas treated with a rate of 50 and 80 mL/min plateaued in 7–8 days and in 4–5 days, respectively. In the ANOVA test, the circulation rate had a significant correlation with variations in CH_4, CO_2, and pH during the experimental period ($p < 0.05$), which confirmed the patterns in Figure 8.

The gas circulation rate did not have any effect on the final upgraded CH_4 content because all the initial CH_4 (60%) was upgraded to about 71% CH_4 regardless of the circulation rate. There was also no significant difference between the effects of different circulation rates on the final upgraded CH_4 content ($p = 0.65$) in the ANOVA test.



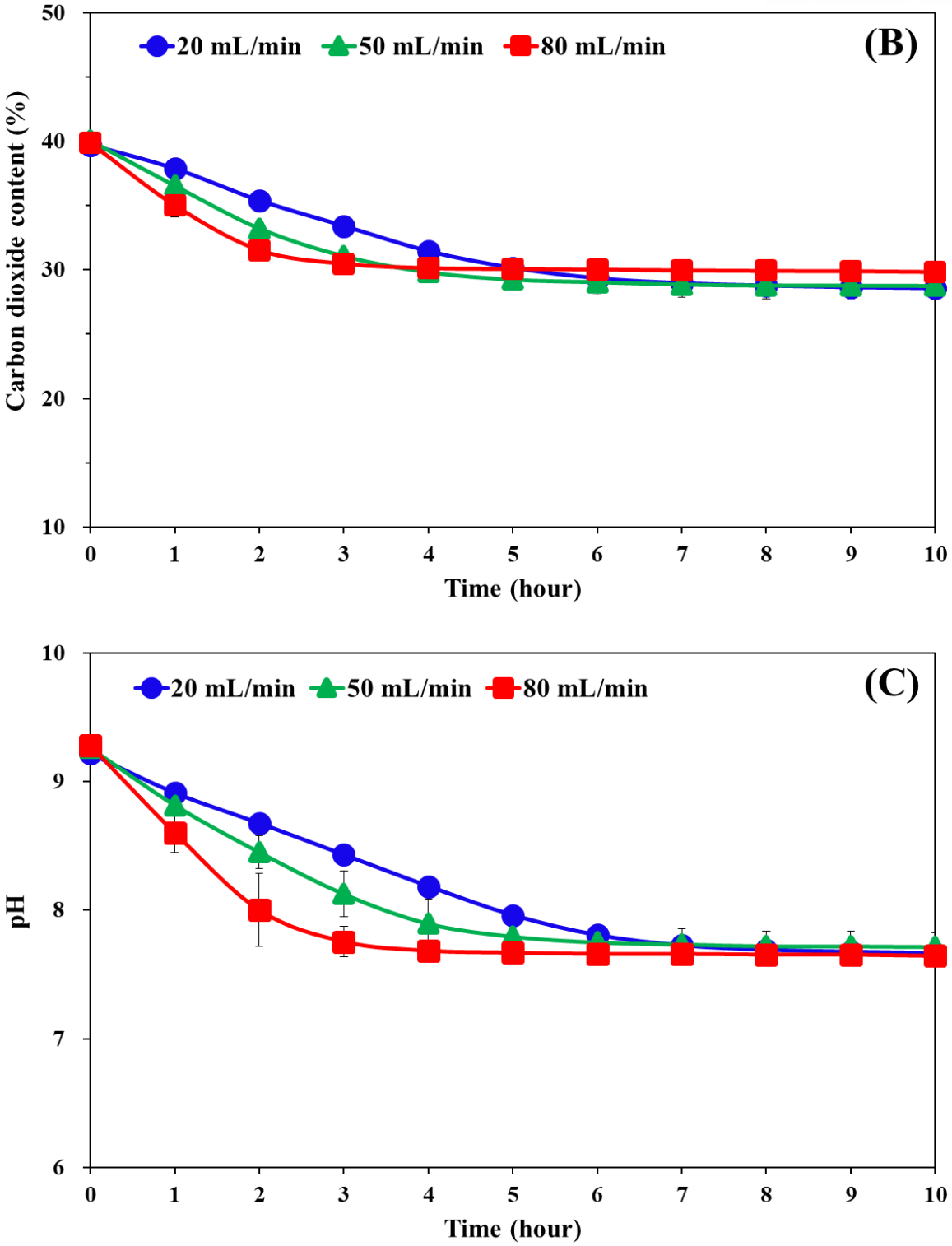
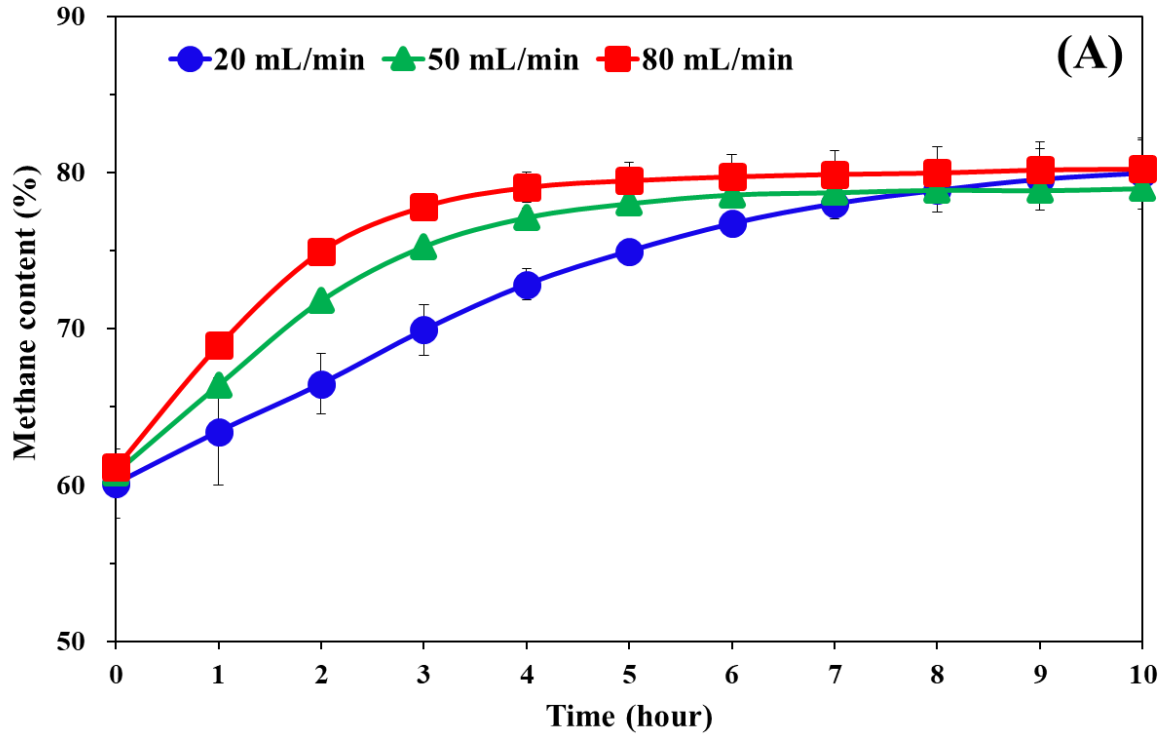
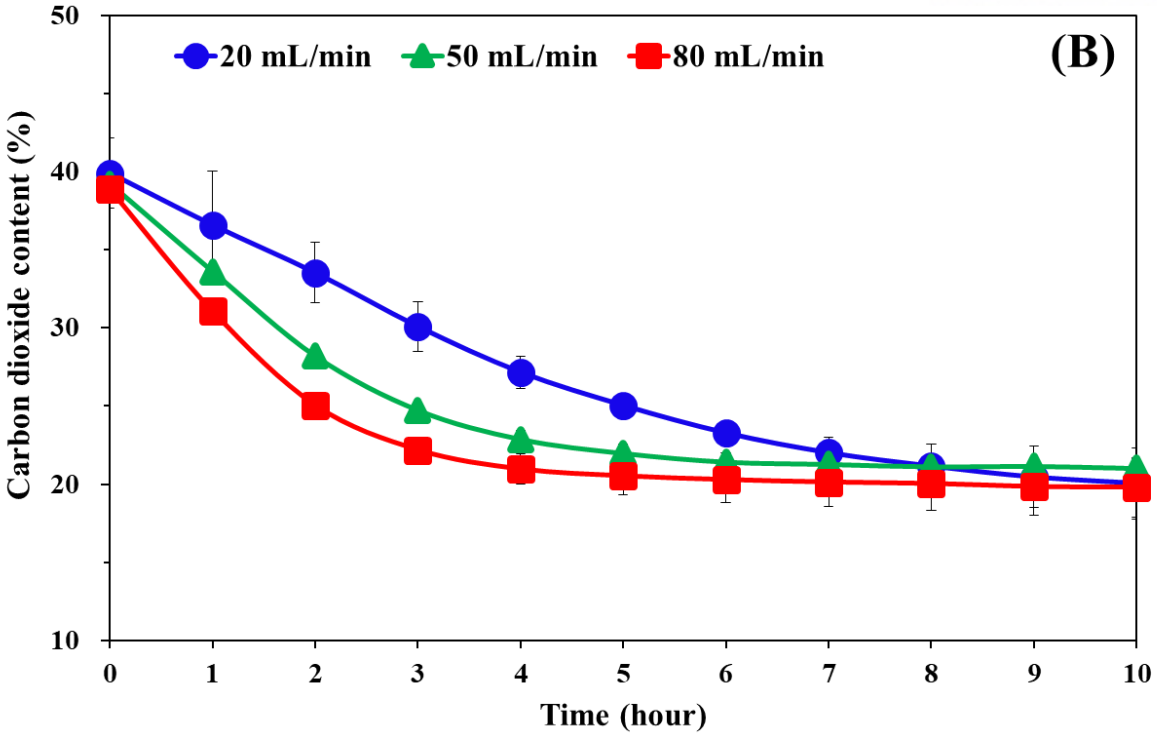


Figure 8. Variations of CH_4 (A), CO_2 (B) and pH (C) in applied 10 L synthetic biogas

The variations in gas composition (%) and pH profile during the upgrade process for 5 L synthetic biogas with hydrolyzed urine are shown in Figure 9. The CH_4 and CO_2 profiles of 5 L biogas reached a plateau state faster with faster circulation rates (Figures 8 A and B), similar to the results obtained from applying 10 L synthetic biogas. However, the initial CH_4 content increased to about 80% at all circulation rates compared with approximately 71% upgraded biogas when 10 L biogas was applied. This suggested that more CH_4 would be upgraded as a higher volume ratio of biogas to urine solvent or a lower volume ratio of solvent to biogas is applied.

Two-way ANOVA supported the above result. The effects of different circulation rates (20, 50, and 80 mL/min) on variations in CH_4, CO_2, and pH ($p < 0.05$) during the experimental period were significantly different and the p values of each dependent variable were much lower than that obtained with 5 L biogas. In addition, there was a significant difference between the effects of 10 L biogas and 5 L biogas on the final upgraded CH_4 content ($p < 0.05$). However, there was no significant difference between the effects of 10 L and 5 L biogas on the final pH value ($p = 0.085$). This statistical result was in agreement with the similar pH values measured after 10 hours, approximately 7.68 for 10 L and 7.85 for 5 L biogas, as shown in Figure 8 C and Figure 9 C.





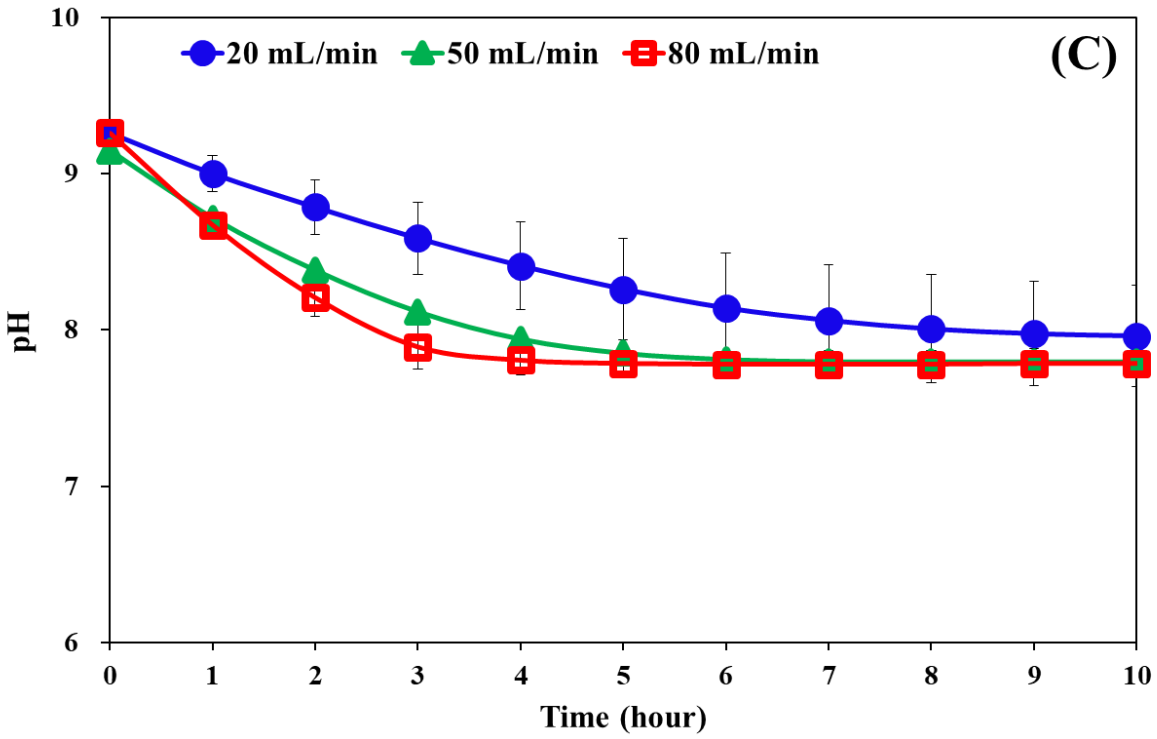


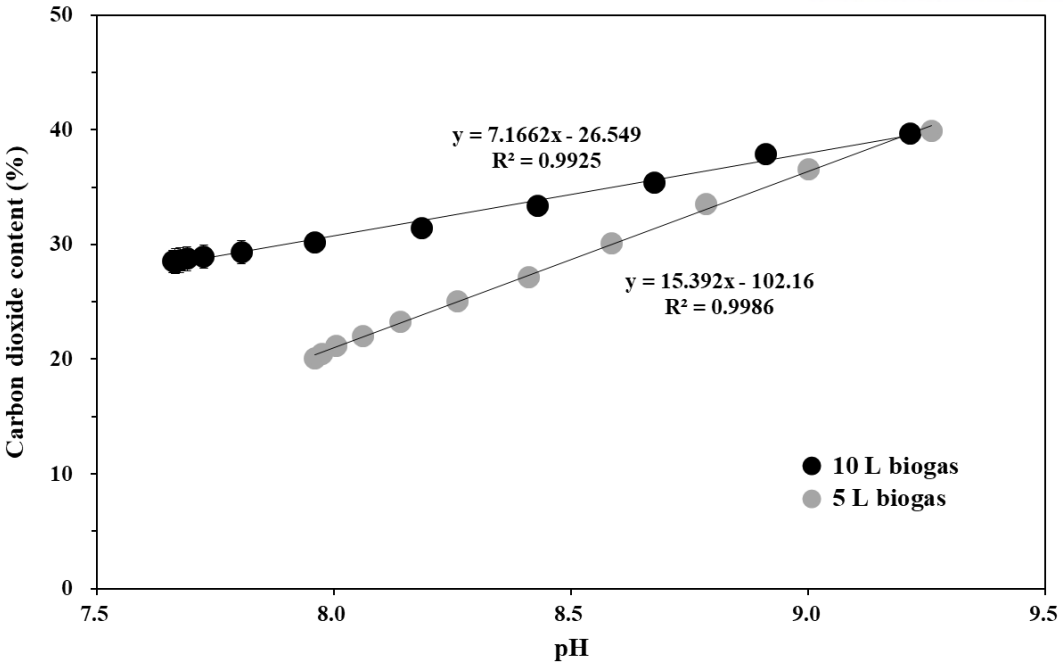
Figure 9. Variations of CH_4 (A), CO_2 (B) and pH (C) in applied 5 L synthetic biogas

The CO_2 removal profile and pH decrease profile were extremely similar at the same circulation rates and applied biogas volumes (Figures 8 B and C; Figures 9 B and C). Therefore, the correlation between CO_2 and the pH profile for the same circulation rate was investigated as seen in Figure 10. For all circulation rates, there were very strong linear corrections between the CO_2 content and the pH profile with both 10 L and 5 L applied biogas because all R^2 values were larger than 0.99. The CO_2 content with 10 L and 5 L biogas seemed to be different at all circulation rates, as seen in Figure 10. The ANOVA results indicated a significant difference in the CO_2 content ($p < 0.05$) according to the biogas volume (10 L and 5 L).

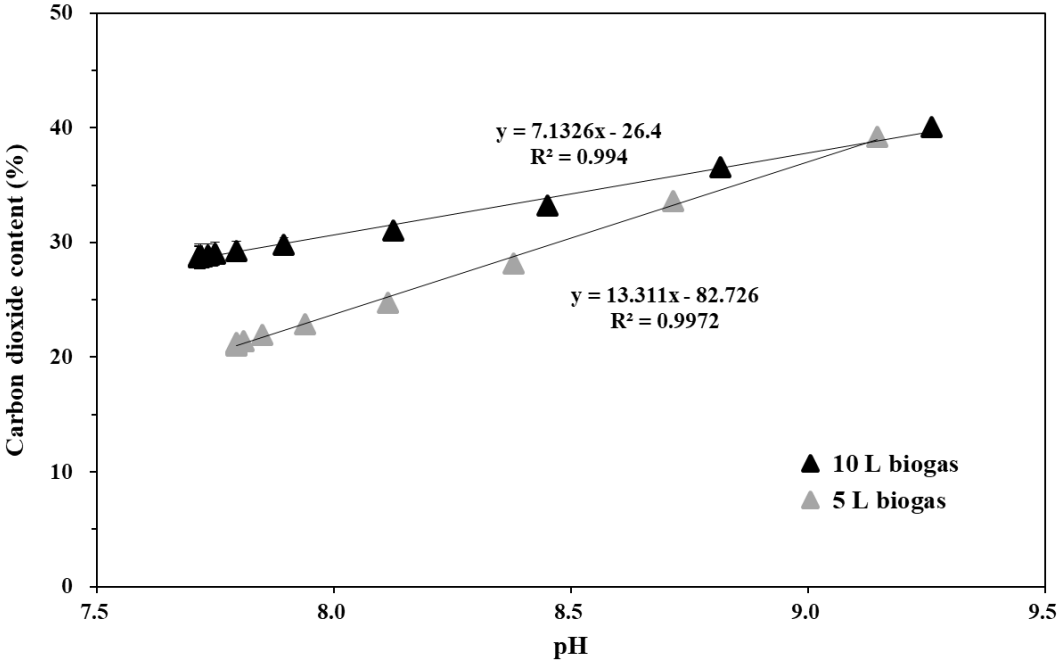
The correlations between the pH profile and the amount of upgraded CH_4 (%), together with the pH profile and the amount of CO_2 (%) removed were investigated at all circulation rates, as shown in Figure 11. There were strong negative correlations between CH_4 (%) and the pH profile and positive correlations between CO_2 (%) and the pH profile. Interestingly, the slope and applied volume seemed to have an inverse relationship. The slope of the correlation between CO_2 (%) and pH almost doubled from approximately 6.6 to 13.2 when the applied volume changed from 10 L to 5 L, as seen in Figure 11 B. It was clear that there was a relationship between the removed CO_2 (or upgraded CH_4) and the volume ratio of biogas applied to the urine solvent. Thus, further investigation of the relationship with the application of various volume ratios is needed.

It can be concluded that pH could play the role of a convenient indicator for identifying the progress of biogas upgrading processes without the need to measure the gas contents because the pH profile has a good linear correction with CH_4 and CO_2 content ($R^2 > 0.95$) regardless of the circulation rates and applied biogas volumes.

(A)



(B)



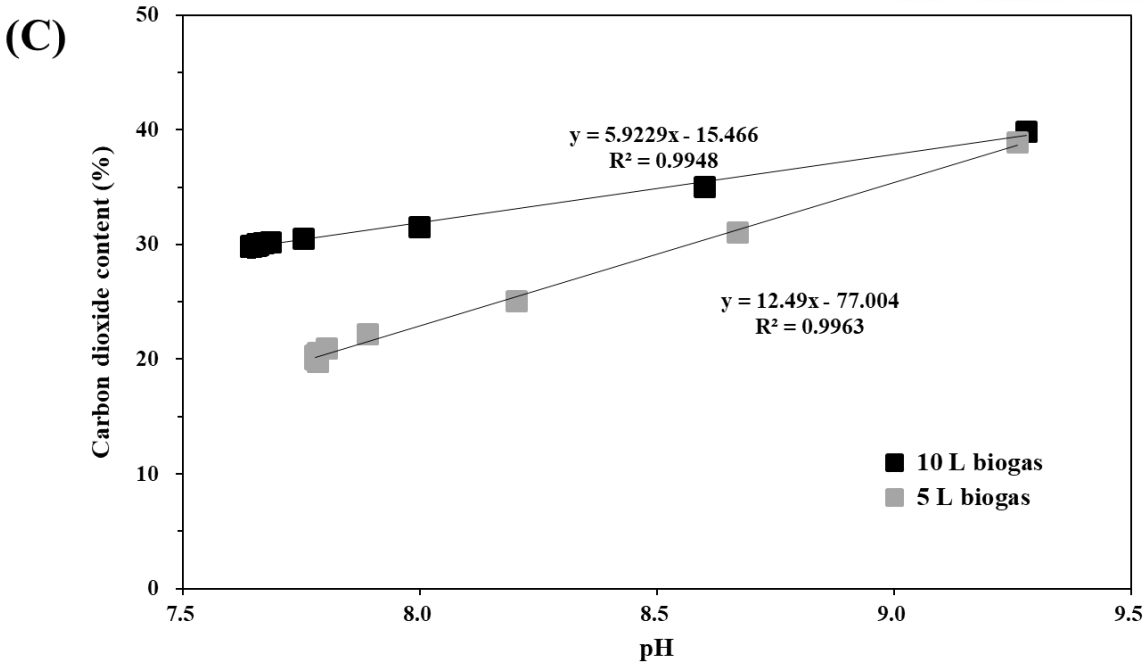


Figure 10. pH and carbon dioxide correlation in 20 (A), 50 (B) and 80 mL/min (C) circulation rate

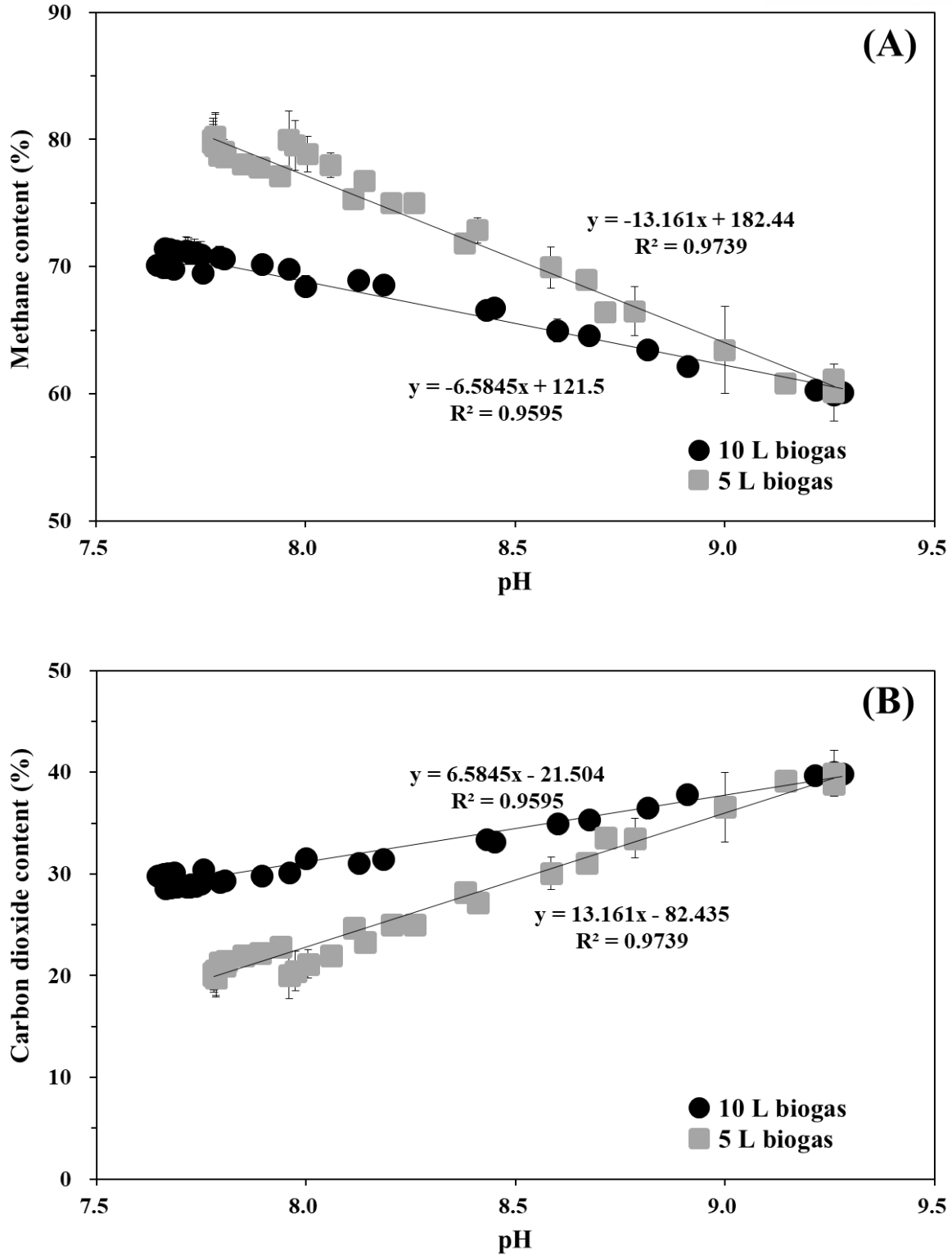


Figure 11. Correlations of pH with methane content (A) and with carbon dioxide content (B)

The ammonia remaining in the treated biogas, the calculated CO_2 removal efficiency, and the CO_2 absorption capacity during synthetic biogas treatment are listed in Table 11. As the volume ratio of biogas to hydrolyzed urine decreased, the CO_2 removal efficiency increased from about 40% to 62%. The removal efficiency increased when a much lower volume ratio was applied.

The absorption capacity decreased from approximately 51 mol CO_2/mol NH_3 to 40 mol CO_2/mol NH_3 as the volume ratio decreased. However, it seems theoretically possible that there is no difference between the capacities regardless of the applied volume ratios. Therefore, further experiments with various volume ratio conditions are needed to investigate the relationship between the removal efficiency and the volume ratio, along with the reason for the different absorption capacities.

The volume ratio of the biogas to urine solvent can be adjusted by changing the volume of the solvent (or reactor), the volume of applied biogas, or the volumes of both the solvent and biogas. The volume ratio was adjusted by changing the applied biogas volume in this study. This approach has an advantage in that it can reduce the reactor size in a batch system. However, it leads to low CO_2 absorption efficiency in a continuous system. Therefore, the volume ratio of biogas to solvent should be optimized for continuous implementation.

Table 11. CO_2 removal efficiency and capacity along with different applied volumes and circulation rates

Volume (L)	Circulation rate (mL/min)	Removed CO_2 (mL)	CO_2 removal efficiency (%)	Ammonia (ppmv)	Capacity (mol CO_2/mol NH_3)
10	20	1711 (5)[a]	43 (0)	2 (0)	0.55
	50	1594 (13)	40 (0)	2 (0)	0.51
	80	1488 (94)	37 (2)	2 (0)	0.48
5	20	1252 (28)	63 (1)	12 (13)	0.40
	50	1183 (36)	59 (2)	23 (10)	0.38
	80	1273 (97)	64 (5)	4 (1)	0.41

[a] Standard deviations are in parentheses.

3.3.2. Upgrading real biogas

To ensure that the biogas upgrading process using hydrolyzed human urine can be applied to actual biogas, real biogas was treated in duplicate using the same hydrolyzed urine (U2) at a circulation rate of 50 mL/min and an applied volume of 5 L. Variations in the gas content and pH profile during the upgrade process for the real biogas are shown in Figure 12. Change patterns similar to those obtained with the 5 L synthetic biogas could be observed, as seen in Figure 9. The initial 62% CH_4 increased to 81%, along with a decrease of CO_2 from 38% to 19%. The results confirmed that the solvent of hydrolyzed urine can be utilized in the real biogas upgrading process.

During the process, hydrogen sulfide (H_2S) decreased from approximately 2700 ppmv to an undetectable range (< 1 ppmv), as shown in Table 12. This is because H_2S is a weak acid and is decomposed at high pH as shown in Equation 16. The pH of fully hydrolyzed urine is approximately 9 (Li and Lancaster Jr, 2013). This is another advantage of using hydrolyzed human urine for upgrading real biogas because H_2S is known to be extremely toxic to life, even at the smallest concentrations, and acute exposure to 500 ppmv can cause death (Li and Lancaster Jr, 2013).

$$H_2S_{(aq)} \leftrightarrow HS^- + H^+ \leftrightarrow S^{2-} + 2H^+ \quad (16)$$

(pK_{a1} = 6.97; pK_{a2} = 12.35 at room temperature)

Although the upgraded 81% CH_4 content in this study is sufficient for use in boilers, further upgrades will be needed for use of biogas as a vehicle fuel, along with the natural gas replacement due to the regulations for CH_4 content (95% >) (Persson et al., 2006). Further studies to develop and optimize the ratio of biogas to solvent, gas circulation rate, type of reactor, and retention time for biogas are required for practical implementation in continuous operation because only one condition, 5 L real biogas with 400 mL of hydrolyze urine, was evaluated in this study.

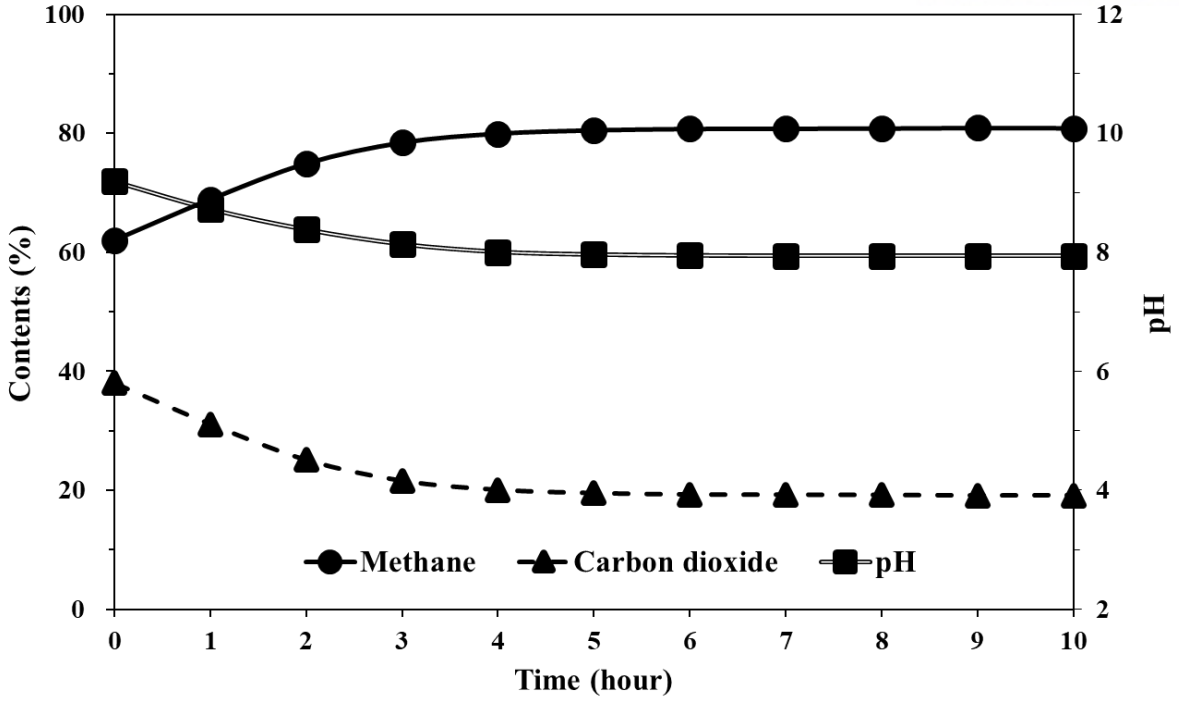


Figure 12. Variations of gas contents and pH profile during treating the real biogas (n = 2)

Table 12. Change of composition in real biogas before and after batch test

Components	Unit	Before batch test	After batch test
CH_4	%	62 (1)[a]	81 (0)
CO_2	%	38 (1)	19 (0)
pH		9.19 (0.03)	7.94 (0.01)
H_2S	ppmv	2736 (7)	nd
NH_3	ppmv	nd[b]	29 (15)

[a] Standard deviations are in parentheses.
[b] Not detected.

3.3.3. Crystalline solids

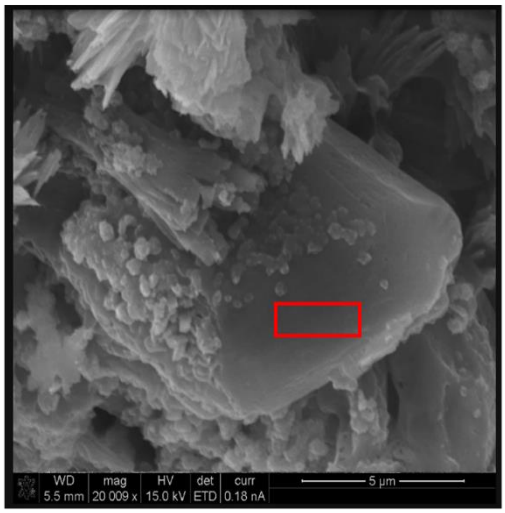
Two major crystalline products that may have existed in the reactor after the biogas upgrading process using hydrolyzed urine are struvite ($MgNH_4PO_4 \cdot 6H_2O$) and ammonium bicarbonate (NH_4HCO_3). A white powder called struvite or magnesium ammonium phosphate hexahydrate (MAP), which can be used as an effective phosphorus fertilizer as the form is solid and it can be transported easily, is spontaneously crystallized during the beginning of urine hydrolysis (Etter et al., 2011). Ammonium bicarbonate, which can also be used as a fertilizer, is the most prevalent solid formed in the CO_2-NH_3 system at room temperature (Sutter and Mazzotti, 2017).

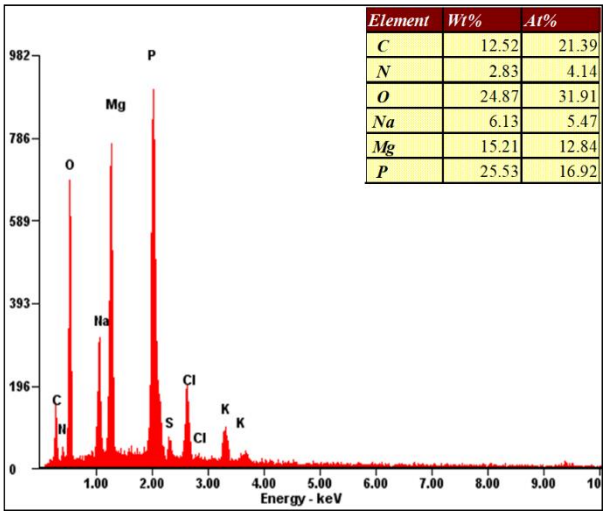
Figure 13 shows SEM images and EDX peaks of the crystalline solids collected after the biogas upgrading test. Unlike other points, the peaks of Mg and P were intense at the points corresponding to a specific crystal structure, as shown in Figures 13 A and B. This might indicate the presence of struvite due to the existence of Mg and P peaks. A similar shape of crystallized struvite in hydrolyzed urine has also been reported (Zhang et al., 2013).

Another SEM pattern in which there were no Mg or P peaks but there were intense C, N, and O peaks was detected, indicating the formation of other solids, as shown in Figures 13 C and D. This might indicate the existence of crystalline ammonium bicarbonate. This is because similar EDX results, which comprised only C, O and N peaks, were reported in another study in which ammonium bicarbonate was produced while synthetic biogas was continuously bubbled through NH_3 solution and the indicative of ammonium bicarbonate was confirmed by XRD (McLeod et al., 2014).

However, the HP-XRD patterns did not confirm the formation of ammonium bicarbonate but only confirmed the formation of struvite, as seen in Figure 14, although the ammonium bicarbonate would be produced. Many impurities formed in hydrolyzed urine such as struvite possibly hindered the formation of ammonium bicarbonate because available NH_4^+ might be consumed. In addition, it was reported that the reaction to produce ammonium carbamate which is three times more soluble than ammonium bicarbonate and so does not readily precipitate was preferred under the condition of low absorption capacity and high pH (Mani et al., 2006). Further research will be required to detect and favor the formation of ammonium bicarbonate because ammonium bicarbonate can be used as an attractive fertilizer and so help to improve the process economics.

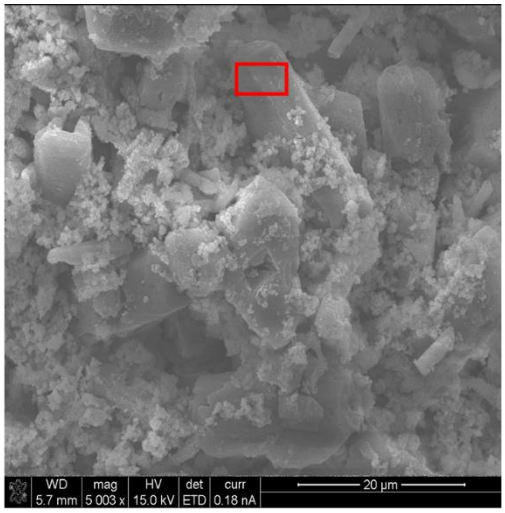
(A)

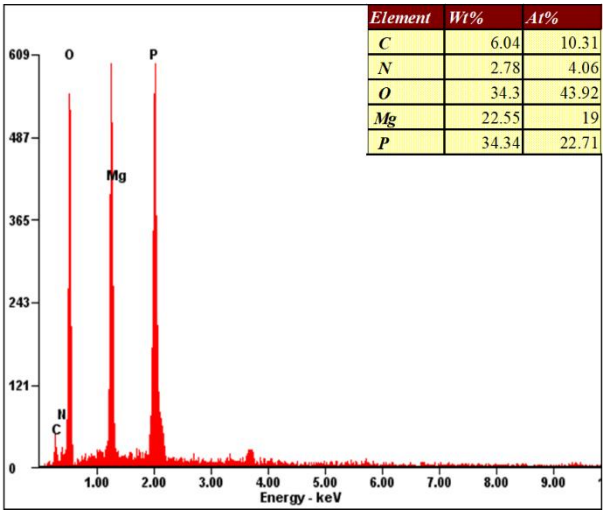




Element	Wt%	At%
C	12.52	21.39
N	2.83	4.14
O	24.87	31.91
Na	6.13	5.47
Mg	15.21	12.84
P	25.53	16.92

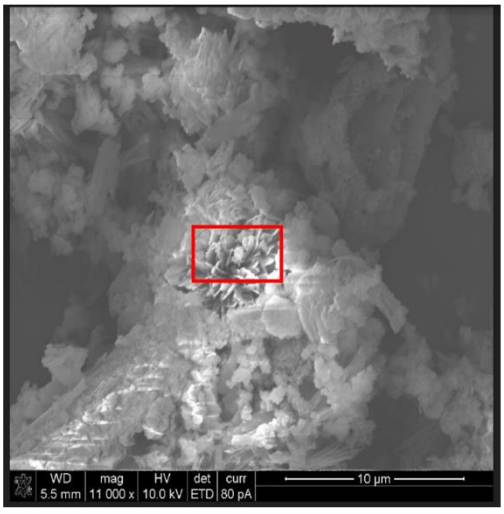
(B)

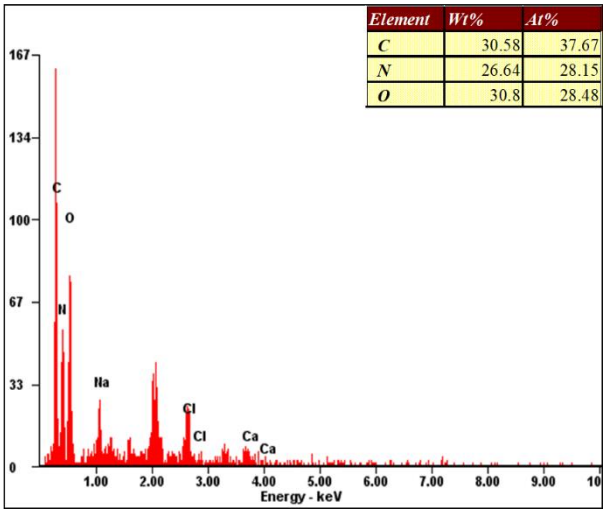




Element	Wt%	At%
C	6.04	10.31
N	2.78	4.06
O	34.3	43.92
Mg	22.55	19
P	34.34	22.71

(C)





Element	Wt%	At%
C	30.58	37.67
N	26.64	28.15
O	30.8	28.48

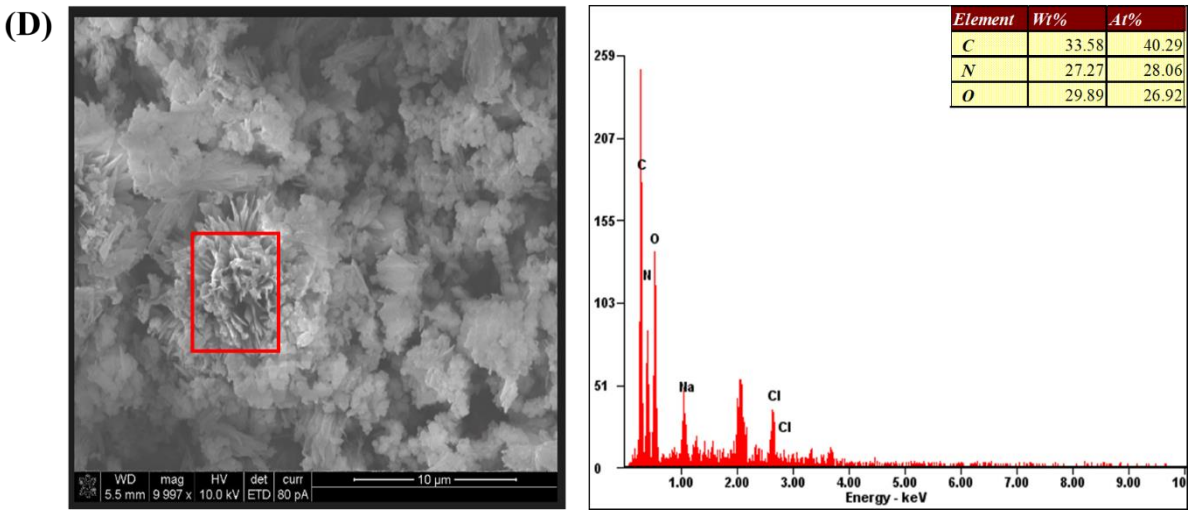


Figure 13. Scanning electron microscope (SEM) images and energy dispersive X-ray (EDX) peaks of solids collected after the biogas upgrading test

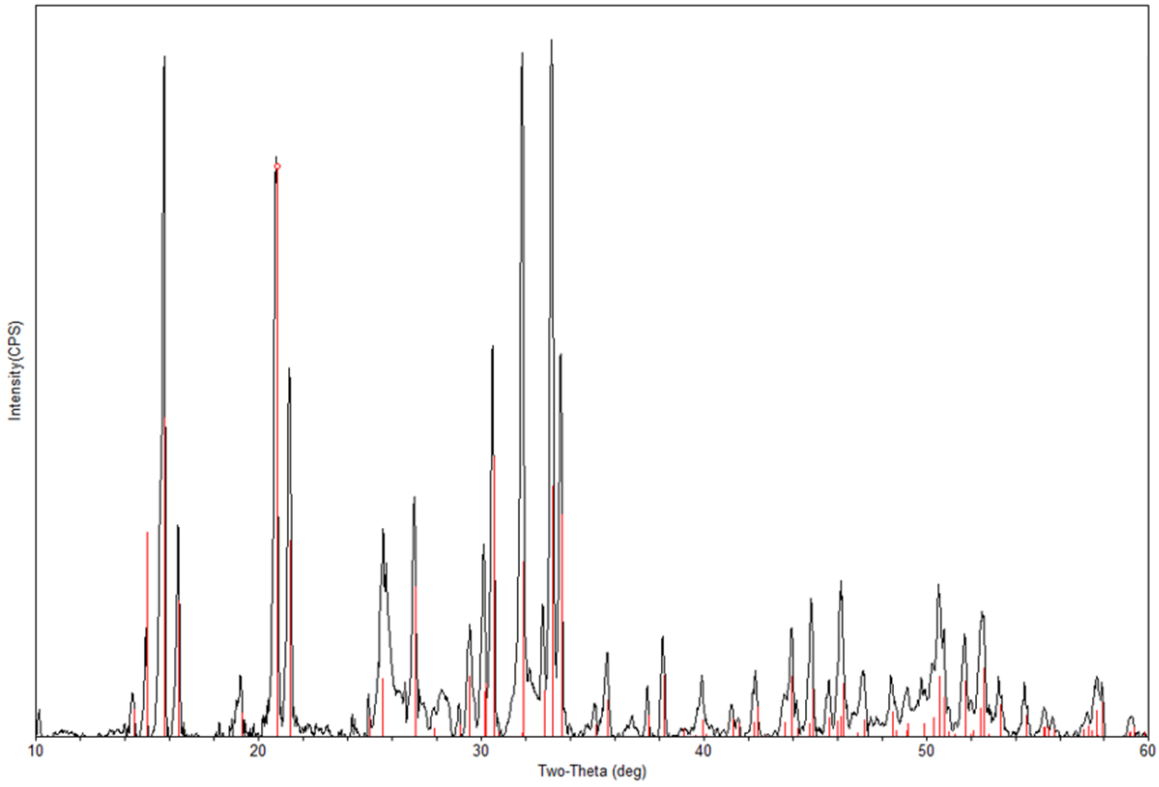


Figure 14. High power x-ray diffraction pattern of solids collected after upgrading test (red color lines mean standard XRD lines of pure struvite)

Chapter 4. Conclusions

Human urine can be used as an inexpensive and competitive new source of ammonia for upgrading biogas as approximately 4,000 mg/ L of total ammonia nitrogen can be produced from urine hydrolysis.

To examine the extent of urine hydrolysis, collected human urine was hydrolyzed under different temperatures and urease concentrations. Urine samples with added urease were hydrolyzed in a short period of time, except for the sample at 4℃. However, urine samples with no urease were hydrolyzed slowly and the temperature had a more dynamic effect on the samples with no added urease. Based on the urine hydrolysis tests, it can be suggested that different strategies, such as the addition of urease and the variation of temperature, can be applied to urine hydrolysis depending on the shape or residence time of the storage tank.

Finally, the potential to use hydrolyzed urine for biogas upgrading was examined in a batch system. The circulation rate affected the length of time required to reach a saturation point but did not affect the upgraded methane content. When 5 L of synthetic biogas was applied, the proportion of CH_4 increased from 60% to 80%. It can be expected that a higher CH_4 content can be obtained as the applied biogas volume decreases or the volume of the solvent increases. When a smaller volume ratio of biogas to urine was applied, CO_2 removal efficiency increased but CO_2 absorption capacity decreased.

The feasibility of using hydrolyzed urine as a solvent for biogas upgrading was confirmed as similar results were obtained when real biogas was applied. The amount of H_2S in real biogas decreased significantly, from 2,700 ppmv to 0 ppmv. This was an additional benefit of using hydrolyzed urine as a solvent because H_2S is harmful to humans.

The overall experimental results suggest that hydrolyzed urine can be effectively used as a solvent to upgrade biogas. Additional upgrading process will be needed to use biogas as vehicle fuel and natural gas replacement. Further studies to optimize the ratio of biogas to solvent, gas circulation rate, type of reactor, and retention time for biogas are also required for practical implementation under continuous operation.

Chapter 5. Further studies

The possibility of using hydrolyzed urine as a new solvent for biogas upgrading was examined in a batch system. Although the upgraded CH_4 content in this study is sufficient for use in boilers, additional biogas upgrading will be required for use of biogas as vehicle fuel and the natural gas replacement.

Further studies are needed to implement a continuous biogas upgrading system in which biogas is continuously upgraded along with a continuous supply of hydrolyzed urine as fertilizers such as ammonium bicarbonate and struvite are simultaneously produced, as shown in Figure 15.

Firstly, further batch mode biogas tests will be performed with more diverse volumes of applied biogas to investigate the optimal point of CO_2 removal efficiency. In addition, the absorption capacity may be theoretically the same regardless of the circulation rates and applied volume ratio of biogas to solvent. However, the calculated absorption capacity was different when 10 L biogas was applied compared to when 5 L biogas was applied. It is expected that the reason for the different results will be revealed with additional batch mode experiments.

Secondly, the performance will be compared in different reactor types and conditions, such as hollow fiber membrane contactor reactors and low temperature maintenance reactors. It is expected that the efficiency under these conditions will be higher because the biogas upgrading test was conducted in batch mode with no temperature control, which mimics the conditions for the most basic type of reactor.

Lastly, ammonium bicarbonate, which is the main product in the CO_2 scrubber using NH_3, will be qualitatively analyzed using other analytical instruments such as FT-IR or Raman spectroscopy. For this process, quantitative analysis of ammonium bicarbonate will also be conducted.

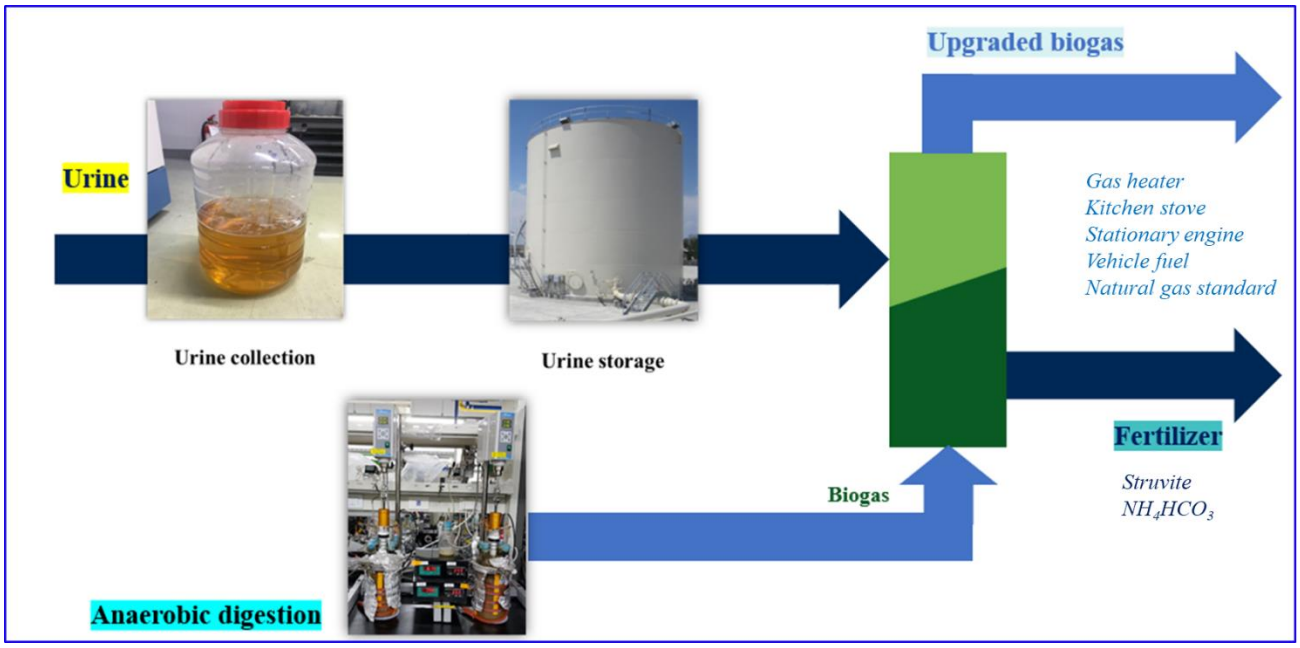


Figure 15. Flow diagram of continuous biogas upgrading process of using human urine

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